

ACTIVITY EFFECTS IN SEAWATER AND  
OTHER SALINE MIXTURES

By

DONALD RICHARD WHITE, Jr.

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By

DONALD RICHARD WHITE, Jr.

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Measurements of electromotive force (EMF) and the isopiestic technique were utilized in the determination of factors which influence the thermodynamic activity and related properties of individual species in complex saline mixtures.

EMF measurements in cells without liquid junction were carried out to determine the mean activity coefficient of HCl,  $\gamma_{\pm}$ , in electrolyte mixtures resembling seawater. In mixtures of HCl-MgCl<sub>2</sub>, it was found that  $\gamma_{\pm}$  decreases in a linear fashion as HCl is replaced by MgCl<sub>2</sub> while maintaining constant total ionic strength and, in this respect, obeys

Harned's Rule. These measurements were carried out at four ionic strengths, namely  $I = 0.1000, 0.3809, 0.6729,$  and  $0.8720 \text{ mol kg}^{-1}$  at nine temperatures from 5 to  $45^\circ\text{C}$ . The three higher ionic strengths correspond to seawater of salinities 20, 35, and  $45^0/00$ . In addition, studies were made on the system  $\text{HCl-NaCl-MgCl}_2$  at  $I = 0.6729$ , the molal ratio of  $\text{NaCl}$  to  $\text{MgCl}_2$  being maintained at 7.202 as in natural seawater. The Harned coefficients obtained from all measurements were found to decrease slowly with temperature. The trace activity coefficients of  $\text{HCl}$ ,  $\gamma_{\pm}^{\text{tr}}$ , were calculated from the Harned equation in two ways. First, by combining Harned coefficients from the  $\text{HCl-MgCl}_2$  study with those from an earlier  $\text{HCl-NaCl}$  study, weighting the two with respect to their relative ionic strength contributions to seawater. Secondly, they were calculated using Harned coefficients from the  $\text{HCl-NaCl-MgCl}_2$  study. All values were found to be identical with those measured earlier in total artificial seawater (excluding sulfate) at all ionic strengths and temperatures included in the experiments.

The concept of single-ion activity and the problem of liquid-junction potentials in pH measurement were addressed in a study of pH in synthetic seawater and saline media simulating serum. Measurements of EMF in a cell with liquid junction at  $25^\circ\text{C}$  were carried out in buffered artificial seawater at salinities of 30, 35, and  $40^0/00$ , each containing a Tris buffer at molalities of 0.02, 0.04, and 0.06.

Comparison of the  $\text{p}m_{\text{H}}$  values calculated by the operational definition with those determined from measurements in cells without liquid junction demonstrates that a residual liquid-junction potential exists which varies with salinity. Within a given salinity, however,  $\text{p}m_{\text{H}}$  values calculated by the operational definition are identical regardless of Tris buffer concentration.

Evidence is presented that pH measurement of blood plasma and other clinical media at ionic strengths of 0.16m vs. the NBS standards may involve residual liquid-junction errors amounting to 0.03 to 0.05 pH unit. EMF measurements of cells both with and without liquid junction indicated that residual liquid-junction effects may be nearly eliminated by matching the ionic strength of the standard to that of the sample. A phosphate buffer composed of 0.005217m  $\text{KH}_2\text{PO}_4$ , 0.018258m  $\text{Na}_2\text{HPO}_4$ , and 0.1m NaCl (buffer ratio 1:3.5 and  $I = 0.16\text{m}$ ) is to be preferred to the NBS phosphate buffer ( $I = 0.1\text{m}$ ) for measurements of this sort.

Isopiestic measurements were carried out at 25°C on mixtures of electrolytes having to do with seawater,  $\text{NaCl-SrCl}_2$  and  $\text{NaCl-Na}_2\text{CO}_3$ , and the resulting osmotic coefficients were determined in the ionic strength range 0.3 to 6.0m. The data were fitted to the current treatments of Pitzer and Scatchard for solutions of mixed electrolytes. Activity coefficients were calculated for the individual solutes in each mixture using the best-fit ion interaction parameters from the Pitzer

treatment. These are discussed in light of the excess free energies of mixing calculated from the corresponding Scatchard parameters.

## CHAPTER 1 INTRODUCTION

When a salt such as sodium chloride is dissolved in water, the resulting solution exhibits a comparatively high electrical conductivity showing that charged ions are present. The thermodynamic properties of the solution may, in part, be described by electrostatic interactions of the ions with each other and by interactions of ions with water molecules. The concentration of the dissolved species in the solvent, and thus the magnitude of these effects, will have a major influence on the thermodynamic activity and related properties.

Classical thermodynamics<sup>1-7</sup> gives a general formula for the chemical potential of any solute,  $i$ , in an ideal solution as:

$$\mu_i = \mu_i^\circ + RT \ln x_i \quad (1.1)$$

where  $x_i$  is the mole fraction of the solute and  $\mu^\circ$  is its chemical potential in the standard state, i.e., when  $x_i$  is unity. The temperature is given by  $T$ , and  $R$  is the gas constant. In an electrolyte solution, however, coulombic ion-ion forces are present and any attempt to measure the chemical potential would result in a departure from equation

1.1, the magnitude of which is a measure of the non-ideality associated with these interactions.

In order to correct equation 1.1, an empirical correction factor may be applied to modify the concentration term:

$$\mu_i = \mu_i^\circ + RT \ln x_i f_i \quad (1.2)$$

This effective concentration term,  $x_i f_i = a_i$ , is termed the activity of the species  $i$ , and  $f_i$  is the "rational" activity coefficient. The concentration may be just as easily expressed in molality,  $m_i$ , where the activity coefficient must take on a different value normally designated by the symbol  $\gamma_i$ . From equation 1.2, it can be seen that the activity must be unity in the standard state. Thus, the standard state on the molality scale is that of a hypothetical solution where the mean ionic molality and activity coefficient are unity, but with the reference state chosen such that  $a_i/m_i = \gamma_i = 1$  when  $m_i$  approaches zero.<sup>8</sup>

The change in the Gibbs free energy of any thermodynamic system as a function of temperature, pressure, and composition is given as:

$$dG = -SdT + VdP + \sum_i \mu_i dn_i \quad (1.3)$$

Therefore, mathematically, the chemical potential of a species  $i$  is the partial derivative of the free energy with respect to moles of  $i$  when temperature, pressure, and moles of other substances remain constant; it is often written as  $\bar{G}_i$ .

$$\bar{G}_i = \left( \frac{\delta G}{\delta n_i} \right)_{T, P, n_j} \quad (1.4)$$

To measure this quantity in an ionic solution, one would need to measure the change in free energy with change in concentration of one ionic species only. Obviously, this would be empirically difficult if not impossible. One can only, therefore, measure the activity coefficient of a net electrolyte, that is at least two ionic species resulting from a single neutral electrolyte.

If one considers a symmetrical electrolyte of the 1:1 charge type, such as HCl, the sum of the chemical potentials of the resulting ions as a function of molality may be given as:

$$\begin{aligned}\bar{G}_{H^+} + \bar{G}_{Cl^-} = & (\bar{G}_{H^+}^{\circ} + \bar{G}_{Cl^-}^{\circ}) + \nu RT \ln (m_{H^+}^{\nu^+} m_{Cl^-}^{\nu^-})^{1/\nu} \\ & + \nu RT \ln (\gamma_{H^+}^{\nu^+} \gamma_{Cl^-}^{\nu^-})^{1/\nu}\end{aligned}\quad (1.5)$$

where  $\nu = \nu^+ + \nu^-$  is the number of ions per molecule of electrolyte and in this case is equal to 2. Defining the respective mean values as:

$$\begin{aligned}\bar{G}_{\pm} &= \frac{\bar{G}_{H^+} + \bar{G}_{Cl^-}}{2} \\ \bar{G}_{\pm}^{\circ} &= \frac{\bar{G}_{H^+}^{\circ} + \bar{G}_{Cl^-}^{\circ}}{2} \\ m_{\pm} &= (m_{H^+}^{\nu^+} m_{Cl^-}^{\nu^-})^{1/\nu} \\ \gamma_{\pm} &= (\gamma_{H^+}^{\nu^+} \gamma_{Cl^-}^{\nu^-})^{1/\nu}\end{aligned}$$

an expression can be written for the mean chemical potential which is, in effect, the average contribution of a mole of ions to the free energy of the system.

$$\bar{G}_{\pm} = \bar{G}_{\pm}^{\circ} + \nu RT \ln m_{\pm} + \nu RT \ln \gamma_{\pm} \quad (1.6)$$



One now has a relation between the free energy of a state in which the ions are infinitely far apart and a state corresponding to a given concentration and its mean activity coefficient,  $\gamma_{\pm}$ , which is experimentally determinable. To split this value of  $\gamma$  into individual ionic activity coefficients will require a theoretical and partly arbitrary approach to be discussed later.

Another way in which the non-ideal behavior of an electrolyte solution may be described is by means of the osmotic coefficient, which may be regarded as a measure of the non-ideality of the solvent due to the presence of ions. It is defined in such a way as to become unity in the pure solvent. A rational activity coefficient for the solvent would fail to emphasize this adequately; since the mole fraction of the solvent is normally so large,  $f_s$  would never deviate much from unity. For this reason, the "rational" osmotic coefficient,  $g$ , is defined by:

$$\ln a_s = g \ln x_s = -g \ln \left( 1 + \frac{vmW_s}{1000} \right) \quad (1.7)$$

where  $W_s$  is the molecular weight of the solvent,  $a_s$  is its activity, and  $m$  is molality. The practical osmotic coefficient,  $\phi$ , on the molality scale is defined by:

$$\ln a_s = \frac{-vmW_s}{1000} \phi \quad (1.8)$$

Therefore, for an aqueous solution for a single electrolyte, equation 1.8 becomes:

$$-55.51 \ln a_w = vm\phi \quad (1.9)$$

In very dilute solutions, the mole fraction of the solute,  $x_i$ , may be described by:

$$x_i = \frac{n_i}{n_w + n_i} \approx \frac{n_i}{n_w} \quad (1.10)$$

where  $n_i$  and  $n_w$  are the number of moles of solute and water, respectively. Therefore from equation 1.9 one finds:

$$v\phi = \frac{-m_w \ln a_w}{m_i} \approx \frac{-\ln a_w}{x_i} \quad (1.11)$$

When  $x_i$  is very small, the last term may be approximated by:

$$\frac{-\ln a_w}{x_i} = \frac{-\ln a_w}{1 - x_w} \approx \frac{\ln a_w}{\ln x_w} \quad (1.12)$$

From this it can be seen that the osmotic coefficient is approximately proportional to the ratio of the logarithms of activity to mole fraction and, in this respect, behaves much like the activity coefficient where  $f_i = a_i/x_i$ .

The relationship between the rational and the molal activity coefficient can be shown<sup>4</sup> to be:

$$f_{\pm} = \gamma_{\pm}(1 + 0.001vW_s m) \quad (1.13)$$

and that between the rational and molal osmotic coefficient as:

$$g \ln x_s = \frac{vmW_s}{1000} \phi \quad (1.14)$$

In the case of any system at equilibrium and maintained at constant temperature and pressure, the sum of the chemical potentials of all species must be zero; as shown by the Gibbs-Duhem relation,

$$n_A d\bar{G}_A + n_B d\bar{G}_B + n_C d\bar{G}_C + \dots = 0 \quad (1.15)$$

where  $n_i$  denotes the number of moles of the  $i$ th species. Therefore, for a solution containing only one solute in water:

$$n_i d\bar{G}_i = -n_w d\bar{G}_w \quad (1.16)$$

The Gibbs-Duhem relation is important in relating the osmotic and activity coefficients. Recalling that:

$$\bar{G}_i = \bar{G}_i^\circ + \nu RT \ln a_i$$

$$\text{and } \bar{G}_w = \bar{G}_w^\circ + RT \ln a_w$$

one can express the Gibbs-Duhem relation as:

$$\nu m \, d \ln (\gamma_\pm m) = -55.51 \, d \ln a_w \quad (1.17)$$

Combining this result with equation 1.9, the osmotic and activity coefficients may be related by:

$$(\phi - 1) \frac{dm}{m} + d\phi = d \ln \gamma_\pm \quad (1.18)$$

and upon integration this may be shown to give:

$$\phi = 1 + 1/m \int_0^m m \, d \ln \gamma_\pm \quad (1.19)$$

Alternatively, activity coefficients can be calculated from osmotic coefficients by expressing the above relationship in the form:

$$\ln \gamma_\pm = (\phi - 1) + \int_0^m (\phi - 1) \, d \ln m \quad (1.20)$$

## CHAPTER 2 ACTIVITY COEFFICIENTS

### Theoretical Background

Electromotive force measurements have been useful in providing a large part of our existing thermodynamic data for electrolyte solutions. They serve as the most common and accurate means by which to view ionic activity.

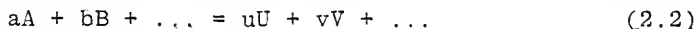
The reaction in a galvanic cell is one in which oxidation and reduction occur simultaneously; that is, electrons are removed from one species which is said to be oxidized and supplied to another species, said to be reduced. The reaction may be regarded as the sum of these two half-reactions, each of which occurs at a respective electrode. If the two electrodes are connected to a voltmeter with a high input resistance, such that no reaction is allowed to occur, the resulting voltage,  $E$ , is a measure of the potential for reaction. This potential is related to the molar free energy change,  $\Delta G$ , for the reaction by:

$$\Delta G = -nFE \quad (2.1)$$

where  $F$  is the Faraday (96,487 coulombs/mole),  $n$  is the number of moles of electrons exchanged, and  $E$  is in volts. The Gibbs energy change is then in joules and is a measure of the

maximum work that the cell reaction can produce. A negative  $\Delta G$  indicates a spontaneous reaction, while a positive  $\Delta G$  indicates the reaction will not occur spontaneously.

Considering the following general chemical reaction:



then the change in free energy which accompanies the reaction is the sum of all the chemical potentials of the products times their respective number of moles minus the same quantities for the reactants:

$$\Delta G = u\bar{G}_U + v\bar{G}_V + \dots - a\bar{G}_A - b\bar{G}_B - \dots \quad (2.3)$$

If one writes for  $\Delta G^\circ$ :

$$\Delta G^\circ = u\bar{G}_U^\circ + v\bar{G}_V^\circ + \dots - a\bar{G}_A^\circ - b\bar{G}_B^\circ - \dots \quad (2.4)$$

and recalls equation 1.1, then:

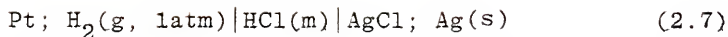
$$\Delta G = \Delta G^\circ + RT \ln \frac{a_U^u a_V^v \dots}{a_A^a a_B^b \dots} \quad (2.5)$$

which is the general form for the free energy of a reaction. Combining relation 2.1 with the above gives the Nernst equation:

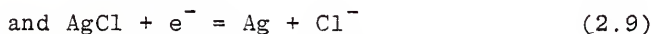
$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_U^u a_V^v \dots}{a_A^a a_B^b \dots} \quad (2.6)$$

which relates EMF to the activities of the various ions. This equation will be used extensively in this work. The term  $E^\circ$  is the standard potential; it is equal to  $E$  when all ions are in their standard states.

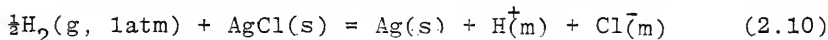
Considering the following galvanic cell<sup>9,10</sup> containing aqueous HCl:



the cell reaction may be regarded as a combination of two half reactions:



which, when combined, give the total cell reaction:



The cell 2.7 is written such that oxidation is taking place at the left electrode, the anode, and reduction takes place at the right, the cathode. A positive EMF, or negative  $\Delta G$ , indicates that the reaction will occur spontaneously as written. The EMF of the cell is given as:

$$E = E^\circ - \frac{RT}{F} \ln a_{\text{H}^+} a_{\text{Cl}^-} \quad (2.11)$$

since hydrogen, silver, and silver chloride are all in their standard states. This may be expanded to give  $E$  in terms of the molalities and mean activity coefficients of the respective species as follows:

$$E = E^\circ - \frac{RT}{F} \ln m_{\text{H}^+} m_{\text{Cl}^-} - \frac{RT}{F} \ln \gamma_{\pm}^2 \quad (2.12)$$

Therefore, it can be seen that EMF measurements are useful in that they easily yield the mean activity coefficient or  $\log \gamma_{\pm}$ :

$$\log \gamma_{\pm} = -\frac{1}{2}[(E - E^\circ)/k + \log m_{\text{H}^+} m_{\text{Cl}^-}] \quad (2.13)$$

where  $k = 2.303RT/nF$ .

### Solutions of Single Electrolytes

A theoretical treatment of the thermodynamic properties of electrolyte solutions must deal with both long-range inter-ionic forces and short-range ion-solvent interactions. The former net effect of attractions and repulsions will tend to decrease the free energy of any particular charged species, manifested in a decrease in the activity coefficient. Also stabilization of ions by solvent molecules tend to lower their free energies. On the other hand, at higher concentration ion-solvent interactions tend to lower the vapor pressure of the solvent, and thus its activity, appearing to increase the activity coefficient of the solute species. There is normally a concentration where these two phenomena are in balance, resulting in an activity coefficient minimum. However, in dilute solutions, interionic forces may be assumed to dominate.

The contribution of electrical interactions with other ions to the free energy of a specified mole of  $j$ -ions is shown<sup>11</sup> to be:

$$\Delta \bar{G}_j(\text{el}) = \frac{-z_j^2 e^2 N}{2\epsilon} \frac{\kappa}{1 + \kappa \bar{a}} \quad (2.14)$$

This arises from the well-known Debye-Hückel formula for the time average potential for an ion of diameter,  $\bar{a}$ , with a charge  $z_j e$ , in the absence of other external forces. The

term,  $\epsilon$ , is the dielectric constant of the medium in which the ions are immersed,  $N$  is Avogadro's number;  $\kappa$  is defined by

$$\left( \frac{8\pi N e^2}{1000 kT} \right)^{1/2} \sqrt{I} \quad (2.15)$$

and is obviously a function of concentration, ionic charge, temperature, and dielectric constant. It is often called the Debye-Hückel reciprocal length since it is this distance,  $\kappa^{-1}$ , at which all of the charge of the ionic atmosphere surrounding a central ion may be considered to be concentrated. The Boltzmann constant,  $k$ , arises from the assumed distribution function.

Assuming that an ionic solution would behave ideally in the absence of these interionic forces, then the partial free energy of a mole of  $j$ -ions may be split into<sup>4</sup>:

$$\bar{G}_j = \bar{G}_j(\text{ideal}) + \Delta\bar{G}_j(\text{el}) \quad (2.16)$$

The term  $\Delta\bar{G}_j(\text{el})$  is essentially the non-ideal contribution containing the activity coefficient, hence:

$$\ln f_j = \frac{\Delta\bar{G}_j(\text{el})}{RT} = \frac{-z_j^2 e^2}{2\epsilon kT} \frac{\kappa}{1 + \kappa a} \quad (2.17)$$

For the mean activity coefficient,  $f_{\pm}$ , which is experimentally determinable:

$$\ln f_{\pm} = \frac{-e^2}{2\epsilon kT} \frac{\kappa}{1 + \kappa a} \frac{v_1 z_1^2 + v_2 z_2^2}{v_1 + v_2} \quad (2.18)$$



The condition of electroneutrality,  $v_1 z_1 = -v_2 z_2$ , allows the following transformation:

$$\ln f_{\pm} = \frac{-|z_1 z_2| e^2}{2\epsilon kT} \frac{\kappa}{1 + \kappa \overset{\circ}{a}} \quad (2.19)$$

Substituting for  $\kappa$ , equation 2.19 can be written in decadic logarithmic form as:

$$\log f_{\pm} = \frac{-A |z_1 z_2| \sqrt{I}}{1 + B \overset{\circ}{a} \sqrt{I}} \quad (2.20)$$

where A and B are constants dependent on T and  $\epsilon$ . The ion-size,  $\overset{\circ}{a}$ , is given in angstroms for numerical convenience.

$$A = \frac{1.8246 \times 10^6}{(\epsilon T)^{3/2}} \quad (2.21)$$

$$B \times 10^8 = \frac{5.029 \times 10^9}{(\epsilon T)^{1/2}} \quad (2.22)$$

At very low concentrations of electrolytes, that is at low  $\sqrt{I}$ , the term  $B \overset{\circ}{a} \sqrt{I}$  becomes negligible compared to unity and equation 2.20 will take the form:

$$\log f_{\pm} = -A |z_1 z_2| \sqrt{I} \quad (2.23)$$

which is known as the Debye-Hückel limiting law. This form is useful in predicting activity coefficient behavior in very dilute solutions. Therefore one could say, with reasonable justification, that the numerator in equation 2.20 is the effect due to long-range coulombic forces, while the denominator brings in modifications for short-range interactions.

By choosing  $3.04 \text{ \AA}$  as a reasonable value of  $\text{\AA}$  for all electrolytes at  $25^\circ\text{C}$ , Güntelberg<sup>12</sup> expressed equation 2.20 simply as:

$$\log f_{\pm} = \frac{-A|z_1 z_2| \sqrt{I}}{1 + \sqrt{I}} \quad (2.24)$$

which is superior to the limiting law, but not adequate above  $I = 0.1\text{m}$ . Guggenheim,<sup>13</sup> by adding an adjustable parameter linear in concentration, improved the equation still further:

$$\log f_{\pm} = \frac{-A|z_1 z_2| \sqrt{I}}{1 + \sqrt{I}} + bI \quad (2.25)$$

### Solutions of Mixed Electrolytes

Studies of mixed electrolytes are important<sup>14-18</sup> from the standpoint that they provide an experimental criterion for judging theoretical predictions. From the bodies of water in the oceans to the biological fluids in the body, solutions of mixed electrolytes are of great importance.

In 1922, Brønsted<sup>19</sup> proposed his theory of specific interaction which states that, "in a dilute solution of constant total concentration, ions will be uniformly influenced by ions of their own sign and specific effects are to be sought in interactions between oppositely charged ions." Employing a modification of the Debye-Hückel expression (equation 2.25) with a term,  $b$ , linear in concentration, Guggenheim continued to build a theory of mixed electrolyte solutions. He introduced specific interaction coefficients,

b, into equations for the activity coefficient of an electrolyte, B, in the presence of another electrolyte, C:

$$\ln \gamma_B = \frac{-1.173\sqrt{I}}{1 + \sqrt{I}} + [2xb_{MX} + (b_{NX} + b_{MY})(1 - x)]m \quad (2.26)$$

Here,  $M^+$  and  $X^-$  are the ions from B and  $N^+$  and  $Y^-$  are the ions of C, both being 1:1 electrolytes in aqueous solution at 25°C. The total molality is m, while xm and (1 - x)m are the molalities of B and C respectively. This form, taken from Robinson and Stokes,<sup>4</sup> describes the activity coefficient and concentration on the molal scale. A similar equation may be written for the electrolyte C:

$$\ln \gamma_C = \frac{-1.173\sqrt{I}}{1 + \sqrt{I}} + [2(1 - x)b_{NY} + (b_{NX} + b_{MY})x]m \quad (2.27)$$

Now, letting  $\gamma'$  refer to the term in brackets on the right of equations 2.26 and 2.27, then when  $x = 0$  and only component C is in solution one can define:

$$\ln \gamma'_{(0)B} = (b_{MY} + b_{NX})m \quad (2.28)$$

$$\ln \gamma'_{C(0)} = 2b_{NY}m \quad (2.29)$$

In contrast, when  $x = 1$ :

$$\ln \gamma'_{B(0)} = 2b_{MX}m \quad (2.30)$$

$$\ln \gamma'_{(0)C} = (b_{NX} + b_{MY})m \quad (2.31)$$

Now it can be seen that:

$$\ln \gamma_B = \ln \gamma_{(0)B} + (\ln \gamma_{B(0)} - \ln \gamma_{(0)B})x \quad (2.32)$$

and similarly for C:

$$\ln \gamma_C = \ln \gamma_{(0)C} + (\ln \gamma_{C(0)} - \ln \gamma_{(0)C})(1 - x) \quad (2.33)$$

Thus, the logarithm of the activity coefficient of either component in a mixture maintained at constant total molality varies linearly with composition.

Harned and co-workers<sup>20-23</sup> have made numerous EMF measurements in solutions of two components at constant ionic strength, and from their results has emerged Harned's Rule:

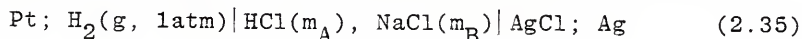
$$\log \gamma_B = \log \gamma_B^\circ - \alpha_B m_C \quad (2.34)$$

which states that the change in  $\log \gamma_B$  from its value in a pure solution of B is linear in molality of the other component. The Harned slope,  $\alpha_B$ , is itself a function of ionic strength. This rule has also been found to be valid for mixtures of non-symmetrical electrolytes as long as the total ionic strength is maintained constant. In this case, the decrease in  $\log \gamma$  of one component is a function of the ionic strength fraction,  $y$ , of the other component.

#### HCl in Seawater

In a mixture such as seawater, composed of many dissolved electrolytes, one could imagine the decrease in  $\log \gamma$  of any single electrolyte to be a function of the respective contributions of the other electrolytes to the total ionic strength.

Macaskill et al.<sup>24</sup> have made measurements of the cell:



where the molalities of the two components were varied while maintaining a constant total ionic strength. The activity coefficient of HCl can be calculated from:

$$\log \gamma_{\text{HCl}} = -\frac{1}{2} [E - E^\circ / k + \log m_{\text{HCl}} (m_{\text{HCl}} + m_{\text{NaCl}})] \quad (2.36)$$

where  $E^\circ$  is the standard EMF of the cell and  $k$  is again written for  $(RT \ln 10)/F$ . The study included three ionic strengths, namely 0.3809, 0.6729, and 0.8720 mol  $\text{kg}^{-1}$  of water, corresponding to seawater with salinities of 20, 35, and 45<sup>0</sup>/00 respectively. It was found that Harned's Rule is indeed valid for these mixtures in the temperature range 5 to 50°C.

By casting the Nernst equation in the following form:

$$\begin{aligned} E + k \log \gamma_{\text{HCl}} &= E^\circ - 2k \log I \gamma_{\text{HCl}}^\circ + 2k \alpha \gamma_{\text{NaCl}} I \\ &= A + B \gamma_{\text{NaCl}} \end{aligned} \quad (2.37)$$

the Harned slope,  $\alpha$ , may be evaluated by the method of least-squares. It is then possible to calculate the trace activity coefficient of HCl using Harned's Rule:

$$\log \gamma_{\text{HCl}} = \log \gamma_{\text{HCl}}^\circ - (\alpha \gamma_{\text{NaCl}}) I \quad (2.38)$$

The trace activity coefficient,  $\gamma_{\text{HCl}}^{\text{tr}}$ , can be calculated in this manner for  $\gamma_{\text{HCl}}$  when  $\gamma_{\text{NaCl}} = 1$ , that is, when NaCl is the only solute; it should approximate the  $\gamma_{\text{HCl}}$  which would actually be measured in a solution of pure NaCl at ionic strength,  $I$ , containing only a trace of HCl. These calculated values of  $\gamma_{\text{HCl}}^{\text{tr}}$  at the various temperatures and ionic strength agree closely with the "trace" activity coefficients actually measured by Khoo et al.<sup>25</sup> with 0.01m HCl in artificial seawater

without sulfate, although they are somewhat higher. From this it may be deduced that the decrease in  $\gamma_{\text{HCl}}$  from  $\gamma_{\text{HCl}}^{\circ}$  is nearly accounted for, in seawater, by the effects of NaCl alone.

A recipe for "sulfate free" seawater suggested by Khoo is as follows:

$$\begin{aligned}\text{NaCl} &= 0.46444\text{m} \\ \text{KCl} &= 0.01058\text{m} \\ \text{CaCl}_2 &= 0.01077\text{m} \\ \text{MgCl}_2 &= 0.05518\text{m}\end{aligned}$$

where m is molality and the ionic strength contribution of  $\text{Na}_2\text{SO}_4$  has been replaced by NaCl. Since KCl and  $\text{CaCl}_2$  are rather minor components, a simpler recipe could be followed in which KCl and  $\text{CaCl}_2$  are replaced by NaCl and  $\text{MgCl}_2$  respectively such that:

$$\begin{aligned}\text{NaCl} &= 0.47502\text{m} \\ \text{MgCl}_2 &= 0.06595\text{m}\end{aligned}$$

The total ionic strength of such a mixture would be 0.67287m (salinity = 35<sup>0</sup>/00) and the corresponding ionic strength fractions are  $y_{\text{NaCl}} = 0.706$  and  $y_{\text{MgCl}_2} = 0.294$  such that  $y_{\text{NaCl}} + y_{\text{MgCl}_2} = 1$ . Now for a three component system such as HCl-NaCl-MgCl<sub>2</sub> in water, a logical extension of Harned's Rule might be:

$$\log \gamma_{\text{HCl}} = \log \gamma_{\text{HCl}}^{\circ} - \alpha_1 y_{\text{NaCl}}^{\text{I}} - \alpha_2 y_{\text{MgCl}_2}^{\text{I}} \quad (2.39)$$

where  $\alpha_1$  is the Harned slope determined by the Macaskill study and  $\alpha_2$  is that to be determined from a similar study of the HCl-MgCl<sub>2</sub> system in a cell identical to 2.35. Equation 2.39 assumes a linear dependence of  $\log \gamma_{\text{HCl}}$  on the ionic

strength fractions of either component. Thus  $(\gamma_{\text{HCl}}^{\text{tr}})_{\text{NaCl/MgCl}_2}$  can be calculated for the case where  $y_{\text{NaCl}} + y_{\text{MgCl}_2} = 1$ , that is:

$$\log(\gamma_{\text{HCl}}^{\text{tr}}) = \log \gamma^\circ - [\alpha_1(0.706) + \alpha_2(0.294)]I \quad (2.40)$$

These calculated values should agree closely with the values of  $(\gamma_{\text{HCl}}^{\text{tr}})_{\text{sw}}$  measured by Khoo if our assumptions are correct and if NaCl and  $\text{MgCl}_2$  are the major influence on the decrease of  $\gamma_{\text{HCl}}$ .

It might also be fruitful to make measurements in a cell of type 2.35 actually containing all three components in water, keeping the ratio  $\text{NaCl/MgCl}_2$  constant as it is in our recipe, and varying only  $(m_{\text{NaCl}} + m_{\text{MgCl}_2})$  with  $m_{\text{HCl}}$  at constant ionic strength. In this case, measurements should yield values of  $\alpha$  that, when put in equation 2.38 with  $y = 1$ , give values of  $\gamma_{\text{HCl}}^{\text{tr}}$  identical to those calculated by 2.40. This was investigated in the present study.<sup>26</sup>

## CHAPTER 3 CONCEPT OF pH

### Theoretical Background

In the preceding chapter we have seen how thermodynamics coupled with experimental practice can provide information concerning mean activities and activity coefficients of electrolytes. However, when it becomes necessary to assign the corresponding values for individual ions one faces a problem for which there is no direct solution.<sup>27,28</sup> This problem manifests itself very clearly in the determination of  $pa_H$  or hydrogen ion activity.<sup>9,29</sup>

Recalling cell 2.7, electromotive force measurements would yield  $E$  in terms of the following:

$$E = E^\circ - k \log a_H^m \gamma_{Cl} \quad (3.1)$$

It is then possible to write an expression for  $pa_H = -\log a_H$  in the following manner:

$$pa_H = \frac{E - E^\circ}{k} + \log m_{Cl} + \log \gamma_{Cl} \quad (3.2)$$

In order to obtain a thermodynamically sound value for  $pa_H$ , a knowledge of  $\gamma_{Cl}$  would be needed. For a conventional representation of this quantity, the Bates-Guggenheim convention<sup>30</sup> was proposed.



Because of the success of the Debye-Hückel equation in fitting activity coefficient data at low ionic strengths, Bates and Guggenheim proposed that the activity coefficient of chloride ion be expressed in the following form at ionic strengths up to 0.1m:

$$\log \gamma_{Cl} = \frac{-A\sqrt{I}}{1 + 1.5\sqrt{I}} \quad (3.3)$$

The choice of the coefficient 1.5 in the denominator is reasonable in that it assigns  $\gamma_{Cl}$  nearly the same value as the mean activity coefficient,  $\gamma_{\pm}$ , for NaCl up to 0.1m. This "convention" has been instrumental in providing a basis for the NBS standard scale for the  $p_{a_H} = pH(S)$  of various dilute buffer substances. If equation 3.2 is cast as follows:

$$p(a_H \gamma_{Cl}) = \frac{E - E^{\circ}}{k} + \log m_{Cl} \quad (3.4)$$

then a plot of this acidity function,  $p(a_H \gamma_{Cl})$ , as a function of  $m_{Cl}$  should be approximately linear. This has been carried out<sup>31,32</sup> for a variety of buffer substances to which chloride has been added, and at the point of intercept,  $p(a_H \gamma_{Cl})^{\circ}$ , equation 3.3 was applied to obtain values of  $pH(S)$ :

$$pH(S) = p_{a_H} = p(a_H \gamma_{Cl})^{\circ} + \log \gamma_{Cl} \quad (3.5)$$

The need for a  $pH(S)$  scale is apparent from the standpoint that it is often desirable to evaluate pH changes with precision greater than 0.1 unit. An internally consistent scale of this sort enables the experimenter to calibrate his pH measuring equipment at pH values both above and below that of the sample by proper choice of NBS standards.

### Cells With Liquid-Junction

In practice, most pH determinations are made using cells of the type:

Reference electrode|KCl(M)||Soln X|Pt; H<sub>2</sub> or glass (3.6)

where the most common reference electrode is the calomel electrode in either 3.5M or saturated KCl. The double vertical lines indicate a liquid junction between solution X and the KCl solution. The cell is first calibrated by employing a pH standard buffer, S, in place of solution X. For this solution, pH(S) is known and the potential,  $E_s$ , between the hydrogen sensing and the reference electrode is recorded. A sample solution of unknown pH is introduced into the cell replacing the standard and a new potential,  $E_x$ , is measured. Ideally, the pH(X) is related to pH(S) and the measured quantities by:

$$\text{pH}(X) = \text{pH}(S) - \frac{(E_x - E_s)F}{RT \ln 10} \quad (3.7)$$

This is the operational definition of pH and provides a simple way in which to relate the pH of an unknown solution to the NBS standard scale. Unfortunately, pH(X) values determined in this manner never fall exactly on the conventional scale because of a residual potential,  $E_j$ , across the liquid junction (vertical lines in 3.6). This potential is a complicated function of the activities and transference numbers of the several ionic species,  $i$ , in the boundary layers of the junction and may be represented by:<sup>9</sup>

$$E_j = -\frac{RT}{F} \int_1^2 \sum_i \frac{t_i}{z_i} d \ln m_i \gamma_i \quad (3.8)$$

where  $t_i$  is the transference number for species  $i$  and  $z_i$  is its charge. An exact evaluation of  $E_j$  is not possible without a knowledge of  $a_H$  which, in turn, is the object of the calculation. This is a dilemma which can only be resolved from "outside the realm of thermodynamics."<sup>16</sup>

The Henderson method<sup>33</sup> of integration of equation 3.8 has been moderately successful in the estimation of the liquid-junction potential. Henderson assumed that the junction consists of a continuous series of mixtures of solutions 1 and 2. The activity of each ion is assumed to be equal to its concentration, and its mobility is constant throughout the junction. The concentration of each species is then given as a function of the concentration in the end solution and the mixing fraction,  $\alpha$ . The transference number is given in terms of concentrations,  $c_i$ , and mobilities,  $\mu_i$ , as:

$$t_i = \frac{c_i' \mu_i}{\alpha \sum_i c_i'' \mu_i + (1 - \alpha) \sum_i c_i' \mu_i} \quad (3.9)$$

Substitution of 3.9 into 3.8 and integration give:

$$E_j = \frac{RT}{F} \frac{\sum_i (\mu_i z_i) (c_i'' - c_i')}{\sum_i \mu_i (c_i'' - c_i')} \ln \frac{\sum_i c_i' \mu_i}{\sum_i c_i'' \mu_i} \quad (3.10)$$

If the ionic mobilities in the two end solutions are taken equal to the mobilities at infinite dilution then one can write:

$$E_j = \frac{RT}{F} \frac{(U_1 - V_1) - (U_2 - V_2)}{(U_1' - V_1') - (U_2' - V_2')} \ln \frac{U_1' + V_1'}{U_2' + V_2'} \quad (3.11)$$

In this equation,  $U$  is  $\sum c_+ \lambda_+^\circ$  and  $V$  is  $\sum c_- \lambda_-^\circ$  for the cations and anions in the end solutions 1 or 2;  $U'$  and  $V'$  are  $\sum c_+ \lambda_+^\circ |z_+|$  and  $\sum c_- \lambda_-^\circ |z_-|$  respectively. The term  $\lambda^\circ$  is the limiting ionic conductivity. The concentrations are in molarity. Equation 3.11 often yields useful estimates of the magnitude and sign of the liquid-junction potentials and is used in this work.

### pH in Seawater

Seawater is a special type of solvent medium in that its pH is regulated within narrow limits. Due to the complete dissociation of the primary electrolyte, NaCl, the ionic strength is high and seawater possesses the favorable characteristics of a "constant ionic medium."<sup>34,35</sup> Media of this sort can be expected to demonstrate minimal changes in  $\gamma_H$  as small changes in chemical composition occur. Furthermore, if pH standards were available which match the ionic strength of seawater, residual liquid-junction potentials would be expected to be minimized. Thus, an experimental scale of  $p_{m_H}$  could be set up rendering the possibility of measuring hydrogen ion concentration in addition to activity. Bates and Macaskill<sup>36</sup> have shown the minor variation in  $\log \gamma_{HCl}$  when NaCl in sulfate-free seawater is replaced by small quantities of HCl at constant ionic strength. In addition, it appears

that seawater of 35<sup>0</sup>/00 salinity indeed effectively nullifies the residual liquid-junction potential.

From the Nernst equation one can derive the following for a cell of type 2.7:

$$E = E^{\circ} - k \log m_{\text{H}^{\text{m}}\text{Cl}} - 2k \log \gamma_{\text{HCl}} \quad (3.12)$$

It is useful to alter the standard state such that the activity coefficient becomes unity at zero molality of HCl in seawater solvent rather than in pure water.<sup>37,38</sup> This is accomplished through the following substitutions in equation 3.12:

$$E^{\circ*} \equiv E^{\circ} - 2k \log \gamma_{\text{HCl}}^{\text{tr}}; \gamma_{\text{HCl}} = \gamma_{\text{HCl}}^{\text{tr}} \gamma_{\text{HCl}}^* \quad (3.13)$$

where  $\gamma_{\text{HCl}}^{\text{tr}}$  is the transfer activity coefficient or medium effect in going from water to seawater and is actually the trace activity coefficient of HCl in seawater. This yields:

$$E + k \log m_{\text{H}^{\text{m}}\text{Cl}} = E^{\circ*} - 2k \log \gamma_{\text{HCl}}^* \quad (3.14)$$

The quantity  $E^{\circ*}$  may be determined by plotting the left side of equation 3.14 as a function of  $m_{\text{HCl}}$  when small quantities of HCl replace NaCl and extrapolating to  $m = 0$ . These types of plots have been found to be straight lines with the slope amounting to only 0.04mV at 0.01 mol kg<sup>-1</sup> of added HCl. In view of this,  $E^{\circ*}$  can be determined routinely with 0.01m HCl with a reasonable estimate of  $\gamma_{\text{HCl}}^*$  at this concentration. By assuming that  $\gamma_{\text{HCl}}^*$  is virtually constant in the seawater medium when small quantities of buffer substances are added

in place of NaCl, as is the case with the addition of HCl, one can determine  $\text{pm}_\text{H} = -\log (m_\text{H})$  from dilute buffer solutions in seawater by measurements of cell 2.7 and the relation:

$$\text{pm}_\text{H} = \frac{E - E^\circ}{k} + \log m_\text{Cl} \quad (3.15)$$

Measurements of this sort have been carried out<sup>25</sup> under these conditions and point to the practicality of a standard  $\text{pm}_\text{H}(\text{S})$  scale in seawater from which values of  $\text{pm}_\text{H}(\text{X})$  could be obtained through use of the operational definition:

$$\text{pm}_\text{H}(\text{X}) = \text{pm}_\text{H}(\text{S}) - \frac{(E_\text{X} - E_\text{S})F}{RT \ln 10} \quad (3.16)$$

Since nullification of the residual liquid-junction potential requires a constant ionic medium and matched ionic strength between the standard buffered seawater and sample, it is of interest to determine the magnitude of liquid-junction errors due to salinity variations. This is investigated in the present study by calibrating a cell of type 3.6 with a buffered seawater at 35<sup>0</sup>/00 salinity where the value  $\text{pm}_\text{H}(\text{S})$  has been determined.<sup>34</sup> Values of  $\text{pm}_\text{H}(\text{X})$  can be calculated by the operational definition from similar measurements above and below 35<sup>0</sup>/00. These results can be compared with pre-determined values from cells without liquid junction.

#### pH in Clinical Media

Measurement of pH in biological fluids is an important part of clinical diagnosis<sup>39,40</sup> and is normally carried out

with a glass electrode assembly in a cell such as 3.6. Standardization of the cell at a point close to the pH of the sample is possible by means of the NBS scale. It is also desirable to match the ionic strength of the standard buffer to that of the sample to minimize residual liquid-junction effects. As was previously shown, the NBS standard buffers are the result of a convention proposed for use at ionic strengths of 0.1m or below and for that reason are more dilute than is desirable for clinical work where the ionic strength is about 0.16m. Attempts<sup>41</sup> have been made to establish primary reference standards at this ionic strength using a solution of Tris-HCl (0.05m), Tris (0.01667m), and NaCl (0.11m); however pH(S) values assigned to this buffer in the usual manner were found to be inconsistent with the NBS scale when compared in cells of type 3.6. Vega and Bates<sup>42</sup> have proposed the use of two substituted ethanesulfonic acids for pH control in the physiological range of pH and at  $I = 0.16m$  which are investigated for their usefulness in the present work.<sup>43</sup>

## CHAPTER 4 OSMOTIC COEFFICIENTS

### Theoretical Background

The isopiestic method is an important tool for studies of electrolytes in solution in that it gives a direct measure of the osmotic coefficient. In making a measurement, a series of solutions containing the salts of interest are allowed to equilibrate with a series of solutions of known vapor pressure at the vapor pressure of water through the vapor phase. The activity of the solvent is related to the vapor pressure,  $p$ , by the following:

$$a_w = p/p^\circ \quad (4.1)$$

where  $p^\circ$  is the partial pressure of pure solvent, in this case, water. Strictly speaking, this relation should be a ratio of fugacities; however, the correction is nearly identical for the numerator and denominator and therefore effectively cancels. When isopiestic vapor equilibrium is attained,  $a_w$  is the same for all solutions. Recalling equation 1.9, the criterion for isopiestic equilibrium is:

$$(\nu m \phi)_{\text{test}} = (\nu m \phi)_{\text{ref}} \quad (4.2)$$

This allows one to calculate  $\phi_{\text{test}}$  directly if  $\phi_{\text{ref}}$  is known. For this reason, a reference solution for which  $\phi$



is known is always equilibrated with the test solutions.

For a mixture of two salts, equation 4.2 is simply:

$$(v_1 m_1 + v_2 m_2) \phi_{\text{test}} = (v m \phi)_{\text{ref}} \quad (4.3)$$

The success of this method depends on three essential factors outlined by Sinclair<sup>44</sup> and mentioned briefly here:

- 1) Good thermal conduction between solutions should be provided in order to ensure solvent transfer rather than a temperature gradient.
- 2) Small quantities of solution nearly at isopiestic equilibrium should be used so that little solvent need actually distill.
- 3) Stirring should be sufficient to allow for maximum diffusion of solute and good heat conduction.

As mentioned in Chapter 1, the osmotic coefficient describes the non-ideal behavior of the solvent. This non-ideality is largely due to the interaction of the electrostatic forces of the ions. Therefore, as a first approximation one can say that  $\phi$  is proportional to the charge density of the solution. This would imply that two solutions, one of NaCl and one of KCl, at the same ionic strength, would have similar osmotic coefficients. This is not the case, however, as a 1 molal solution of NaCl has a  $\phi$  value of 0.967 while at the same concentration of KCl,  $\phi = 0.897$ . In this sense, the solvent activity must be controlled by other more specific forces dependent on the nature of the ions. In general, one might say that two salts of the same charge type generate

different osmotic coefficients as a consequence of specificities in cation-anion interactions and/or different hydration characteristics.

### Solutions of Single Electrolytes

Since the work of Debye and Hückel<sup>11</sup> there have been several advances<sup>45</sup> in explaining theoretically the behavior of electrolytes at appreciable concentrations. However, only in the last two decades has extensive correlation of experimental data with theory resulted in useful semi-empirical treatments.<sup>18,46-50</sup>

From equation 2.20 for the logarithm of the activity coefficient according to Debye and Hückel, we have, on changing the symbolism slightly,<sup>47,51</sup>

$$\ln \gamma_{\pm} = \frac{S |z_+ z_-| \sqrt{I}}{1 + A \sqrt{I}} \quad (4.4)$$

where now  $S = -1.17202$  is the Debye limiting slope at 25°C,  $|z_+ z_-| = Z$  is the charge factor, and  $A$  is the adjustable term  $B^\circ$ . If this relationship is differentiated, substituted into equation 1.19, and integrated analytically, the following expression for the osmotic coefficient,  $\phi$ , is obtained:

$$\frac{\nu m \phi}{I} = 1 + \frac{SZ}{A^3 I} \left[ (1 + A \sqrt{I}) - \frac{1}{(1 + A \sqrt{I})} - 2 \ln (1 + A \sqrt{I}) \right] \quad (4.5)$$

For higher concentrations, where this equation would normally fail, additional arbitrary terms may be added in higher powers of ionic strength, such that:

$$\frac{vm\phi}{I} = 1 + \frac{SZ}{A^3 I} [(1 + A\sqrt{I}) - \frac{1}{(1 + A\sqrt{I})} - 2 \ln (1 + A\sqrt{I})] \\ + BI + CI^2 + DI^3 + EI^4 \quad (4.6)$$

The corresponding equation for the activity coefficient can be written:

$$\ln \gamma_{\pm} = \frac{SZ}{1 + A\sqrt{I}} + (2B)I + (3/2C)I^2 + (4/3D)I^3 + (5/4E)I^4 \quad (4.7)$$

Equation 4.6 can be applied to osmotic coefficient data for solutions of single electrolytes and the parameters A through E evaluated by the method of least-squares. The parameters are chosen such that the sum squared of  $\phi$  observed minus  $\phi$  calculated or  $\sum (\phi_{\text{obs}} - \phi_{\text{calc}})^2$  is minimized over the ionic strength range. The parameters can then be tabulated for a variety of electrolytes. It is possible to employ these data in Scatchard's neutral-electrolyte treatment for electrolyte mixtures.<sup>50,52</sup> Although this method represents the osmotic and activity coefficients accurately for many pure electrolyte systems, there is little promise of a simple physical interpretation of the parameters obtained in this way.

Pitzer, on the other hand, has taken a somewhat different approach in seeking to use fewer parameters, each of which retains as much physical meaning as possible. By modification of the Debye-Hückel equation in the manner of Rasaiah and Friedman<sup>53,54</sup> and using a three-term power series expansion, he derives a rigorous expression which relates the osmotic coefficient to an "electrostatic" term plus a

series of virial coefficients, each of which is a peculiar and purely theoretical function of ionic strength.<sup>46</sup>

In these terms, the properties of single electrolyte solutions take the following forms for an electrolyte MX:

$$\phi - 1 = |z_+ z_-| f^\phi + m(2\nu_M \nu_X / \nu) B_{MX}^\phi + m^2 [2(\nu_M \nu_X)^{3/2} / \nu] C_{MX}^\phi \quad (4.8)$$

where 
$$f^\phi = \frac{A^\phi \sqrt{I}}{1 + 1.2\sqrt{I}}, \quad A^\phi = -0.392$$

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-2\sqrt{I})$$

It can be seen that  $f^\phi$  is the electrostatic term coming directly from the Debye-Hückel theory; it reduces to the limiting slope for osmotic coefficients (-0.392) at low concentrations. The parameter  $B_{MX}^\phi$  represents interactions between ions of like charge and may be represented by a linear term,  $\beta_{MX}^{(0)}$ , plus a second term,  $\beta_{MX}^{(1)} \exp(-2\sqrt{I})$ . This function has the property of a rapid change with  $\sqrt{I}$  at low ionic strengths and a smooth approach to a constant value at high ionic strengths. The third parameter,  $C_{MX}^\phi$ , represents triplet interactions involving two ions of like charge and one of opposite charge and is certain to be small in magnitude. An expression analogous to equation 4.8 may be written for the activity coefficient, with appropriate changes in these virial coefficients:

$$\ln \gamma_\pm = |z_+ z_-| f^\gamma + m(2\nu_M \nu_X / \nu) B_{MX}^\gamma + m^2 [2(\nu_M \nu_X)^{3/2} / \nu] C_{MX}^\gamma \quad (4.9)$$

where

$$f^Y = A^\phi [\sqrt{I}/(1 + 1.2\sqrt{I}) + (2/1.2) \ln (1 + 1.2\sqrt{I})]$$

$$B_{MX}^Y = B_{MX}^\phi + 1/I \int_0^1 B_{MX}^\phi(x) dx$$

$$C_{MX}^Y = 3/2 C_{MX}^\phi$$

Thus, osmotic coefficient data fitted to equation 4.8 may be converted readily into activity coefficient data for the solute.

### Solutions of Mixed Electrolytes

In seeking to describe the variation of osmotic coefficients of mixtures of electrolytes, two noteworthy treatments have been used extensively, namely Scatchard's neutral-electrolyte<sup>50,52,55-57</sup> treatment and the equations of Pitzer.<sup>46,58-60</sup>

As mentioned above, Scatchard's equations for mixtures of electrolytes result directly from single electrolyte equations 4.6 and 4.7 where the Debye-Hückel theory was extended using power-series terms in ionic strength. Rearrangement of Scatchard's general equation for the osmotic coefficient of a mixture of two 1:1 electrolytes in water yields the following:

$$\begin{aligned} 2\phi = 2\phi_A^\circ y_A + 2\phi_B^\circ y_B + y_A y_B I(b_{01} + b_{02}I + b_{03}I^2) \\ + (y_A - y_B)y_A y_B I(b_{12}I + b_{13}I^2) \end{aligned} \quad (4.10)$$

where  $\phi_j^\circ$  is the osmotic coefficient in the pure single electrolyte solution derived from equation 4.6,  $y_j$  is the ionic

strength fraction of component  $j$ , and the terms  $b_{ij}$  are various mixing parameters. Osmotic coefficients obtained from such mixtures in conjunction with the best-fit parameters from equation 4.6 may be used to evaluate the mixing parameters,  $b_{ij}$ , by the method of least-squares. Corresponding equations can also be written for the activity coefficients of the individual species, which may be calculated from the appropriate forms when these mixing parameters are available. Similarly, one can express the osmotic coefficient for a mixture of 1:1 and 1:2 electrolytes in water by:

$$(1 + y_A)\phi = 2\phi_A^0 y_A + \phi_B^0 y_B + \text{mixing terms} \quad (4.11)$$

Pitzer's general equation for electrolyte mixtures is not readily reduced to terms in  $\phi^0$  and  $y$  for the single electrolytes. For a solution composed of two electrolytes MX and NX with a common ion X, with no restriction on charge, his equation rather takes the form:

$$\begin{aligned} \phi - 1 = [2/(m_M + m_N + m_X)] \{ & I\phi^0 + m_M m_X B_{MX}^{\phi} + m_N m_X B_{NX}^{\phi} \\ & + m_M m_N (\theta_{MN} + I\theta'_{MN}) + |z_X/z_M|^{1/2} m_M m_X^2 C_{MX}^{\phi} \\ & + |z_X/z_N|^{1/2} m_N m_X^2 C_{NX}^{\phi} + m_M m_N m_X \psi_{MNX} \} \end{aligned} \quad (4.12)$$

where  $\theta_{MN}$  and  $\psi_{MNX}$  arise from a consideration of additional interactions among combinations of ions. The term  $\theta'_{MN}$  arises from the dependence of  $\theta_{MN}$  on ionic strength and is expected to be small. The other terms are identical to those in equation 4.8 and are determined from data on the single electrolyte solutions, MX and NX.

## CHAPTER 5 EXPERIMENTAL

### Electromotive Force Measurements

#### Materials

Purified hydrochloric acid for the EMF measurements was obtained by distilling reagent grade (Fisher) HCl, retaining the middle fraction from each of two distillations. The product was analyzed gravimetrically for chloride by precipitation of AgCl using a standard procedure.<sup>61</sup> Results of analysis indicated 5.63600 mol chloride per kg (air weight) of stock solution. A secondary stock ( $0.186625 \text{ mol kg}^{-1}$  solution) was prepared by dilution and this was used in preparation of the mixtures.

A solution of magnesium chloride was prepared by dissolving reagent grade (Mallinckrodt)  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  in water to make a solution approximately 1.5 molal. The resulting solution was analyzed gravimetrically to yield a stock solution  $3.04958 \text{ mol kg}^{-1}$  in chloride.

Sodium chloride was purified by twice recrystallizing reagent grade (Mallinckrodt) NaCl from water and drying the product at  $300^\circ\text{C}$  prior to use. Stock solutions were prepared by weighing the dried solid.

Phosphate buffer solutions for the pH measurements were prepared from the NBS Standard Reference Materials:  $\text{KH}_2\text{PO}_4$ , SRM186Ic, and  $\text{Na}_2\text{HPO}_4$ , SRM186IIc. The solids were dried overnight at  $110^\circ\text{C}$  prior to use and the solutions prepared by weighing the dried solids and adding degassed water according to standard procedure.<sup>9</sup>

Buffers of N-tris(hydroxymethyl)methyl-2-aminoethanesulfonic acid (TES) and a N-2-hydroxyethylpiperazine-N'-2-ethanesulfonic acid (HEPES) were prepared from the commercial solids (Sigma) which had been recrystallized twice from 80% ethanol-water and dried at  $80^\circ\text{C}$  in a vacuum desiccator. Each was then weighed accurately into a glass-stoppered flask to which was added an appropriate amount of standardized NaOH solution. Dried NaCl was then added as necessary to achieve the desired ionic strength.

Standard carbonate-free sodium hydroxide solution was prepared by dilution of a 50% (wt/wt) NaOH solution with degassed water. It was standardized by titrating with primary standard grade (NBS SRM84h) potassium acid phthalate.

A buffer solution of tris(hydroxymethyl)aminomethane (Tris) was prepared from a solution of the primary standard grade (Sigma) base to which was added standard HCl solution and the appropriate amount of NaCl.

Potassium chloride for the synthetic seawater solutions was reagent grade (Mallinckrodt) which had been recrystallized twice from water and dried overnight at  $120^\circ\text{C}$ . Solutions were prepared by weighing the dried solid.



A stock solution of calcium chloride was prepared from reagent grade (Matheson, Coleman, and Bell)  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  by dissolving the salt in water to make a solution approximately 2.0m. The solution was analyzed gravimetrically, and the results indicated  $2.73604 \text{ mol kg}^{-1}$  solution.

Sodium sulfate was reagent grade (Fisher) anhydrous  $\text{Na}_2\text{SO}_4$  dried at  $120^\circ\text{C}$  in vacuo for at least 6 hours. A stock solution was prepared by weighing the dried solid.

Water used in the preparation of all solutions was de-ionized in a central building source and redistilled in our laboratory from an all-glass still. For buffer solutions the water was degassed either by boiling or bubbling  $\text{N}_2$ .

Hydrogen gas was obtained in a commercial cylinder and purified by passage over a platinum "DeOxo" catalyst prior to introduction into the cells.

Silver oxide for the preparation of the silver-silver chloride electrodes was prepared by addition of a solution of sodium hydroxide to silver nitrate solution as described by Bates.<sup>9</sup> The precipitate was washed 30 times with distilled water.

Platinizing solution for the hydrogen electrodes was prepared by dissolving 2 grams of hexachloroplatinic acid in 100ml of 2M HCl.

Mercury for the calomel electrode was commercial instrument mercury (Bethlehem) triply distilled in continuous vacuum. The calomel was reagent grade (Fisher)  $\text{Hg}_2\text{Cl}_2$ .

### Preparation of Cell Solutions

All solution mixtures were prepared by weighing and combining stock solutions containing a known amount of each substance such that the desired mole ratios were achieved. The stock solutions were made sufficiently concentrated so that water was always added as a last step to reach the desired ionic strength. Weighings were performed on a Sartorius 5-decimal or a Mettler 3- or 4-decimal balance as appropriate such that accuracy was always better than 1 part in ten thousand. Vacuum corrections were made in all weighings.

For the  $\text{HCl-MgCl}_2$  mixtures,  $\text{HCl}$  was weighed into a tared glass-stoppered erlenmeyer flask and the amount of  $\text{MgCl}_2$  needed to achieve approximate mole fractions of 0.9, 0.7, 0.5, 0.3, and 0.1 in  $\text{MgCl}_2$  was added. One solution of pure  $\text{HCl}$  was prepared at each of the ionic strengths. The quantities of  $\text{HCl}$  stock weighed out initially were such that the final solutions would weigh about 100 grams. This procedure was carried out to give solutions at four ionic strengths, namely 0.1000, 0.3809, 0.6729, and  $0.8720 \text{ mol kg}^{-1}$ .

Three-component mixtures of  $\text{HCl-NaCl-MgCl}_2$  were prepared similarly from  $\text{HCl}$  stock and a solution of  $\text{NaCl}$  and  $\text{MgCl}_2$  of a fixed molal ratio,  $\text{NaCl/MgCl}_2 = 7.202$ . Four solutions were prepared in which  $\text{NaCl}$  and  $\text{MgCl}_2$  together contributed fractions of approximately 0.5, 0.3, 0.1, and 0.0 to the total ionic strength,  $I = 0.6729 \text{ mol kg}^{-1}$ .

The compositions of the buffer solutions used for pH measurements are given in Table 5. In cases where buffer and/or the NaCl concentration was varied, the buffer was appropriately diluted and NaCl added by weighing the dried solid.

Synthetic seawater solutions buffered with an equimolal Tris buffer were prepared at salinities of 40, 35, and 30<sup>0</sup>/00 with three buffer concentrations, 0.06, 0.04, and 0.02m, at each salinity. This was achieved by combination of a concentrated seawater stock solution containing less than the desired amount of NaCl, a stock solution of NaCl, and an equimolal Tris:Tris-HCl buffer. The synthetic seawater stock solution was prepared according to the recipe given by Khoo *et al.*, such that if all of the required NaCl had been added the salinity would have been greater than 45<sup>0</sup>/00. The solutions were prepared by weighing out an aliquot of this seawater stock and calculating the amount of water necessary to dilute it to the desired salinity. Appropriate quantities of Tris:Tris-HCl and NaCl solutions were then added by weight and finally the mixture diluted with water. It should be noted that Tris:Tris-HCl was added at the expense of NaCl to maintain the proper chloride content.

#### Preparation of Electrodes

The hydrogen electrodes were made from platinum foil approximately 1cm<sup>2</sup> in area, spot-welded to a platinum wire sealed in glass tubing. The foil was platinized in a

solution of 2% (wt/vol) chloroplatinic acid in 2M HCl by electrolyzing at about 30mA for 5 minutes. Care was taken such that no bubbles formed at the electrode surface during electrolysis. The electrodes were stored in distilled water and cleaned after use by boiling in "aqua regia."

The silver-silver chloride electrodes were of the thermal-electrolytic type<sup>9</sup> and were prepared by thermal decomposition of a paste of silver oxide and water formed at the base of the electrode. The base was a helix of No. 26 platinum wire about 2mm in diameter sealed in glass tubing. The surface of the silver formed was then converted to silver chloride by electrolysis in 1M HCl. The electrodes were stored in dilute (0.1M) NaCl and, after use, were cleaned by boiling in concentrated nitric acid. Following preparation, the electrodes were checked for bias by measuring the EMF of each electrode versus an arbitrary reference electrode. Any bias was taken into account in the measurements.

The calomel electrode in the cell with liquid junction was prepared with 3.5M KCl. A mercury pool about 1cm deep was formed in the right-hand half cell and was covered with a 2mm layer of calomel which had been wetted with the KCl solution. The cell compartment was carefully filled to the 14/20 ground glass joint at the top and a platinum wire sealed in glass tubing with a 14/20 adaptor was carefully lowered through the KCl solution and calomel into the mercury to avoid mixing of the layers. The cell compartment

was completely filled with KCl solution prior to this step to exclude all air and create an airtight seal at the joint.

### Equipment and Procedures

The cell without liquid junction is shown in Figure 1 and is described by Gary, Bates, and Robinson.<sup>62</sup> It is an all-pyrex cell except for teflon stopcocks. A three-stage saturation process takes place in the compartments to the right of the electrodes and insures that no change in solution composition will occur in the electrode compartments due to the passage of hydrogen gas.

The cells were first flushed with hydrogen to remove any traces of oxygen. The solutions, also deaerated and saturated with hydrogen, were then introduced into the cell via the y-tube, care taken so as not to introduce oxygen. The electrodes were then placed into their respective compartments. The cells were supported in brass frames and placed in a water bath; temperature control to  $\pm 0.01^\circ\text{C}$  in the range  $5 - 50^\circ\text{C}$  was provided. Purified  $\text{H}_2$  was allowed to bubble constantly through the saturator over the hydrogen electrode and out of the gas trap. The measurements were shown to be consistent after 2 hours at  $25^\circ\text{C}$ , at which time the temperature was lowered. Equilibrium was reattained rapidly, within 30 minutes, and the next measurement recorded. This procedure was followed at  $5^\circ$  intervals to  $5^\circ\text{C}$ , and then the temperature was cycled upward to  $25^\circ\text{C}$  where

Figure 1. EMF cell without liquid junction



the original measurement was checked for reproducibility. Measurements were then made at 5° intervals to 50°C and back to 25°C for a final reading. Cell measurements obtained in this manner demonstrated excellent reproducibility, within 0.04mV, when EMF's were corrected to standard 1 atmosphere pressure.

The cell with liquid junction is shown in Figure 2. A calomel electrode was prepared in the right-hand compartment, and the KCl solution was constantly renewed. The left-hand compartment was equipped with a gas tube through which pre-saturated  $H_2$  was bubbled over the electrode. The electrode was seated in a 14/20 ground-glass joint. Gas was allowed to escape through the gas trap. Solutions that had been deaerated and saturated with  $H_2$  were introduced into the left-hand compartment followed by the electrode, care being taken to avoid air. The KCl solution being the heavier, formation of the liquid-junction above the 3-way stopcock was permitted. A water jacket completely surrounded the cell compartments, and each solution was allowed to thermally equilibrate for 1 to 2 hours. After formation of the junction, the calomel and hydrogen electrodes were connected to a digital voltmeter and the EMF recorded when it appeared stable, usually within 5 minutes. Inasmuch as the EMF was not always reproducible from day to day, all measurements were normalized to a fixed value for a phosphate reference buffer, measurements of which were constantly repeated throughout the course of the experiments.



Figure 2. EMF cell with liquid junction



## Isopiestic Measurements

### Materials

Strontium chloride was purified by twice recrystallizing reagent grade (Mallinckdrodt)  $\text{SrCl}_2$  from slightly acidified water. A stock solution was prepared and analyzed gravimetrically for chloride. The results indicated 1.63068 mol  $\text{SrCl}_2$  per kg solution.

Sodium carbonate (Fisher) was heated at  $300^\circ\text{C}$  for 24 hours to drive off  $\text{H}_2\text{O}$  and was then dissolved in degassed water to yield 1.65165 mol  $\text{kg}^{-1}$  solution.

Sodium chloride for use as the isopiestic reference was recrystallized twice from water and dried at  $300^\circ\text{C}$ . Solutions were made by weighing the dried solid.

### Preparation of Solutions

All solution mixtures were prepared by combining stock solutions by weight to achieve the desired mole ratios. The water was previously degassed to minimize sputtering of the solutions when they were subjected to vacuum. The  $\text{NaCl-SrCl}_2$  and the  $\text{NaCl-Na}_2\text{CO}_3$  mixtures were prepared by identical methods, with the ionic strength fraction of the second component,  $y_B$ , varying from 0.17 to 0.85. The solution with the highest  $y_B$  also necessarily had the highest ionic strength. The exact compositions of the solutions are given in Tables 10 and 13.

### Equipment and Procedures

The apparatus for the isopiestic measurements consists of a vacuum desiccator containing up to 12 gold-plated silver cups. The cups, containing 2 to 3 grams of solution, were seated on a copper block 2.5cm thick to ensure thermal equilibration. The desiccator was slowly evacuated to a pressure of about 25 torr, carefully avoiding sputtering of the solutions. The entire desiccator was then immersed in a water bath maintained at  $25 \pm 0.01^\circ\text{C}$  and was rocked gently by mechanical means. Stirring was accomplished by the use of either glass beads or platinum gauze in each cup. Concentrated solutions ( $>1\text{m}$ ) required only 3 days to a week to reach equilibrium, while more dilute solutions would require up to 2 weeks. Duplicate cups were run, that is, 2 cups for each solution. At the end of the equilibrating period, the cups were weighed on a microbalance. Knowing the weight of the solid in each cup and the weight of the cup, the initial calculation was a measure of wt. solid/wt. solution from which the molality of each solution was determined. Equilibrium was assumed complete when this result agreed within 0.1% between 2 cups containing identical solutions. Following the weighings, the cups were returned to the desiccator and the amount of water necessary to dilute the solutions to a lower ionic strength was calculated and added dropwise with a graduated syringe. The system was then re-evacuated and the procedure repeated until the desired ionic strength range was covered.

## CHAPTER 6

### RESULTS

#### Electromotive Force Measurements

##### Standard Potential of the Silver-Silver Chloride Electrode

Before analyzing results from EMF Measurements in a cell of type 2.7, one needs to evaluate the quantity  $E^\circ$  in the Nernst equation, that is, the standard potential of the silver-silver chloride electrode. It has been discovered that values of  $E^\circ_{\text{Ag;AgCl}}$  determined in different laboratories lead to varying results, presumably due to variations in preparative techniques.<sup>63</sup> For this reason, routine standardization should be continued, and such determinations have been made in the present work.

From the Nernst equation describing the EMF of cell 2.7, one can write:

$$E = E^\circ - \frac{4.605RT}{nF} (\log m_{\text{HCl}} - \log \gamma_{\text{HCl}}) \quad (6.1)$$

As pointed out in Chapter 2,  $\log \gamma_{\text{HCl}}$  can be accurately represented at low concentrations by an equation of the form:

$$-\log \gamma_{\text{HCl}} = \frac{A m^{1/2}}{1 + m^{1/2}} - \beta m \quad (6.2)$$

where A is the constant of the Debye-Hückel limiting law for a particular temperature. Thus, from equation 6.1, one has:

$$E + 2k \left( \log m_{\text{HCl}} - \frac{Am^{1/2}}{1 + m^{1/2}} \right) = E^\circ - \beta m \quad (6.3)$$

A plot of the left side of equation 6.3 as a function of  $m$  should give a straight line with an intercept of  $E^\circ$ . Bates and Bower<sup>64</sup> have tabulated values of  $E^\circ$  at various temperatures based on extrapolations of this sort, only with the inclusion of the ion-size parameter which can be varied to give the best fit of the data. Having obtained the best values for  $E^\circ$ , one can then return to equation 6.1 and calculate values of  $\log \gamma_{\text{HCl}}$ . Considering cell 2.7 containing 0.01 mol kg<sup>-1</sup> HCl, one may express the standard potential as:

$$E^\circ = E + 2k \log (0.01) \gamma_{\text{HCl}} \quad (6.4)$$

Thus,  $E^\circ$  may be calculated over a range of temperatures from one measurement only at each temperature, with a knowledge of  $\gamma_{\text{HCl}}$  at that concentration. Table 1 gives the values of  $E$  and  $E^\circ$  obtained from measurements of this sort in the temperature range 5 to 45°C. Values of  $E^\circ$  from Bates and Bower's extrapolations are given for comparison.

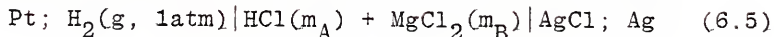
#### Activity Coefficient of HCl in Seawater

In an attempt to elucidate activity coefficient behavior of HCl in saline mixtures approximating seawater,<sup>65,66</sup> EMF measurements have been carried out in mixtures of HCl-MgCl<sub>2</sub> and HCl-NaCl-MgCl<sub>2</sub>. The sodium and magnesium chlorides, the major salt components of seawater,<sup>67</sup> exert a substantial influence on the observed behavior.

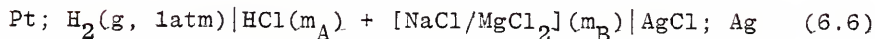
Table 1. Values of E and  $E^\circ$  for the Cell:  
 Pt;  $H_2|HCl(0.01m)|AgCl; Ag$

<u>t(°C)</u>	<u>E (V)</u>	<u><math>E^\circ</math> (V)</u>	<u><math>E^\circ</math> (V)</u> <sup>64</sup>
5	+0.45951	+0.23410	+0.23413
10	0.46091	0.23141	0.23142
15	0.46216	0.22857	0.22857
20	0.46325	0.22556	0.22557
25	0.46417	0.22238	0.22234
30	0.46498	0.21907	0.21904
35	0.46565	0.21566	0.21565
40	0.46615	0.21208	0.21208
45	0.46665	0.20836	0.20835

The measurements were made in cells of the type:



and



where  $m_A$  and  $m_B$  are respectively the molality of HCl and the molality of added  $\text{MgCl}_2$  or the mixture  $\text{NaCl}/\text{MgCl}_2$ . In the first case, the ratio of acid to salt was varied while the total ionic strength was kept constant. The measurements were carried out in this manner at four ionic strengths, namely 0.1, 0.3809, 0.6729, and  $0.8720 \text{ mol kg}^{-1}$ . The three higher ionic strengths correspond to seawater of salinities 20, 35, and  $40^0/00$ . In the second series of measurements, the ternary mixture  $\text{HCl}-\text{NaCl}-\text{MgCl}_2$  was investigated, where the ratio of HCl to total salt was varied at an ionic strength of  $I = 0.6729 \text{ mol kg}^{-1}$  ( $S = 35^0/00$ ). The molal ratio of  $\text{NaCl}/\text{MgCl}_2$  was always kept constant at 7.202, which would be the same ratio as in seawater consisting of only those two salts. All measurements were made at nine temperatures, 5 to 45 C. The results of all of the EMF measurements are given in Table 2.

The  $\text{HCl}-\text{MgCl}_2$  mixtures have a total ionic strength given by  $I = m_A + 3m_B$ . The ionic strength fraction,  $y_B$ , of  $\text{MgCl}_2$  is:

$$y_B = 3m_B/I \quad (6.7)$$



Table 2. Electromotive Force of Cells of Type 2.7 Containing HCl-MgCl<sub>2</sub> Mixtures and HCl-NaCl-MgCl<sub>2</sub> Mixtures From 5 to 45°C, in Volts

$y_B$	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C	45°C
	HCl-MgCl <sub>2</sub> : Ionic strength = 0.1000 mol kg <sup>-1</sup>								
0.9000	0.41929	0.42001	0.42063	0.42106	0.42133	0.42149	0.42151	0.42132	0.42113
0.7001	0.33060	0.33082	0.33090	0.33083	0.33060	0.33025	0.33977	0.33918	0.33844
0.5000	0.37622	0.37618	0.37600	0.37569	0.37520	0.37459	0.37384	0.37300	0.37201
0.3001	0.36618	0.36598	0.36562	0.36512	0.36446	0.36367	0.36277	0.36174	0.36057
0.09931	0.35831	0.35789	0.35747	0.35684	0.35605	0.35511	0.35407	0.35291	0.35161
0	0.35499	0.35458	0.35403	0.35334	0.35248	0.35151	0.35040	0.34918	0.34785
	HCl-MgCl <sub>2</sub> : Ionic strength = 0.3809 mol kg <sup>-1</sup>								
0.9000	0.35856	0.35833	0.35791	0.35735	0.35664	0.35580	0.35487	0.35380	0.35263
0.6999	0.32955	0.32881	0.32787	0.32679	0.32558	0.32426	0.32282	0.32124	0.31954
0.4999	0.31486	0.31386	0.31267	0.31133	0.30987	0.30830	0.30660	0.30478	0.30283
0.3001	0.30457	0.30339	0.30202	0.30052	0.29889	0.29712	0.29525	0.29325	0.29113
0.09983	0.29643	0.29512	0.29361	0.29197	0.29021	0.28833	0.28632	0.28420	0.28195
0	0.29289	0.29153	0.28996	0.28826	0.28644	0.28449	0.28242	0.28024	0.27792
	HCl-MgCl <sub>2</sub> : Ionic strength = 0.6729 mol kg <sup>-1</sup>								
0.9000	0.33135	0.33066	0.32983	0.32881	0.32771	0.32650	0.32515	0.32370	0.32211
0.7000	0.30205	0.30084	0.29949	0.29797	0.29636	0.29464	0.29278	0.29082	0.28874
0.4999	0.28702	0.28554	0.28394	0.28213	0.28011	0.27833	0.27622	0.27400	0.27168
0.3001	0.27636	0.27472	0.27294	0.27100	0.26897	0.26680	0.26452	0.26213	0.25964
0.1001	0.26789	0.26611	0.26420	0.26213	0.25997	0.25767	0.25526	0.25274	0.25012
0	0.26422	0.26239	0.26042	0.25826	0.25608	0.25372	0.25126	0.24869	0.24602
	HCl-MgCl <sub>2</sub> : Ionic strength = 0.8720 mol kg <sup>-1</sup>								
0.9000	0.31837	0.31745	0.31640	0.31522	0.31393	0.31235	0.31097	0.30932	0.30756
0.7000	0.28884	0.28741	0.28586	0.28410	0.28236	0.28029	0.27840	0.27625	0.27397
0.5000	0.27358	0.27190	0.27009	0.26815	0.26610	0.26376	0.26163	0.25922	0.25670
0.2999	0.26270	0.26086	0.25888	0.25676	0.25451	0.25200	0.24970	0.24713	0.24444
0.1001	0.25404	0.25206	0.24994	0.24770	0.24533	0.24269	0.24026	0.23754	0.23472
0	0.25027	0.24823	0.24606	0.24375	0.24133	0.23880	0.23616	0.23340	0.23055
	HCl-NaCl-MgCl <sub>2</sub> : Ionic strength = 0.6729 mol kg <sup>-1</sup>								
0.5000	0.28369	0.28212	0.28042	0.27858	0.27660	0.27450	0.27232	0.27004	0.26763
0.3000	0.27443	0.27274	0.27089	0.26892	0.26680	0.26458	0.26227	0.25984	0.25737
0.09998	0.26734	0.26554	0.26359	0.26140	0.25927	0.25696	0.25454	0.25200	0.24934
0	0.26427	0.26244	0.26046	0.25831	0.25606	0.25371	0.25125	0.24867	0.24596

Thus, both  $m_A$  and  $m_B$  can be calculated from the values of  $I$  and  $y_B$  given in Table 2. For the ternary mixtures where  $m_{NaCl} = 7.202m_{MgCl_2}$ , the total ionic strength is given by:

$$I = m_A + 1.2348m_B \quad (6.8)$$

where 
$$y_A = 1.2348m_B/I \quad (6.9)$$

Mean ionic activity coefficients of HCl,  $\gamma_A$ , in the presence of  $MgCl_2$  are easily calculated from the Nernst equation expressed in terms of  $y_B$ :

$$\log \gamma_A = \frac{E^\circ - E}{2k} - 0.5 \log (1 - y_B)(1 - y_B/3)I^2 \quad (6.10)$$

and for the ternary mixtures:

$$\log \gamma_A = \frac{E^\circ - E}{2k} - 0.5 \log (1 - y_B)(1 - 0.09802y_B)I^2 \quad (6.11)$$

Just as in equation 2.37, the Harned slope may be calculated by the method of least-squares for any given values of  $I$  and  $y_B$ . With modification for HCl- $MgCl_2$ , the equation takes the form:

$$\begin{aligned} E + k \log (1 - y_B)(1 - y_B/3) &= E^\circ - 2k \log I\gamma_A^\circ + 2k\alpha y_B I \\ &= A + By_B \end{aligned} \quad (6.12)$$

where  $A$  and  $B$  are determined by linear regression analysis.

For the ternary mixture, equation 6.12 takes the form:

$$E + k \log (1 - y_B)(1 - 0.09802y_B) = A + By_B \quad (6.13)$$

The results for  $\alpha$  ( $=B/2kI$ ) and  $\log \gamma_A^\circ$  are given in Table 3, along with the standard deviations of fit at each temperature and ionic strength. Values of the temperature variation of  $\alpha$ ,  $d\alpha/dT$ , are given at the foot of Table 3.

Table 3. Values of  $-\log \gamma_A^\circ$  and the Harned Coefficient ( $\alpha$ ) for the Systems HCl-MgCl<sub>2</sub> and HCl-NaCl-MgCl<sub>2</sub> as a Function of Ionic Strength at 5 to 45°C

T° C	HCl-MgCl <sub>2</sub>			HCl-MgCl <sub>2</sub>			HCl-MgCl <sub>2</sub>		
	$-\log \gamma_A^\circ$	$\alpha$	$10^4 s^a$	$-\log \gamma_A^\circ$	$\alpha$	$10^4 s$	$-\log \gamma_A^\circ$	$\alpha$	$10^4 s$
5	0.0948	0.0569	3	0.1132	0.0503	3	0.1005	0.0509	3
10	0.0956	0.0576	4	0.1156	0.0492	4	0.1032	0.0498	4
15	0.0968	0.0550	4	0.1174	0.0483	4	0.1060	0.0489	4
20	0.0980	0.0519	3	0.1195	0.0472	4	0.1087	0.0479	4
25	0.0993	0.0493	3	0.1220	0.0456	4	0.1123	0.0462	4
30	0.1005	0.0483	3	0.1245	0.0441	3	0.1155	0.0456	4
35	0.1015	0.0456	3	0.1266	0.0432	3	0.1186	0.0443	4
40	0.1030	0.0375	2	0.1291	0.0416	3	0.1220	0.0434	5
45	0.1044	0.0362	3	0.1316	0.0408	4	0.1257	0.0418	4
$\frac{d\alpha}{dT} = -0.000552$				$-0.000247$			$-0.000224$		

<sup>a</sup> s = standard deviation for regression.

Table 3 - extended

HCl-MgCl <sub>2</sub>		HCl-NaCl-MgCl <sub>2</sub>	
I = 0.8720		I = 0.6729	
$-\log \gamma_A^\circ$	$\frac{\alpha}{10^4 s}$	$-\log \gamma_A^\circ$	$\frac{\alpha}{10^4 s}$
0.0865	0.0504	0.1012	0.0428
0.0898	0.0492	0.1040	0.0406
0.0930	0.0481	0.1066	0.0389
0.0965	0.0468	0.1091	0.0384
0.1002	0.0462	0.1124	0.0362
0.1033	0.0441	0.1157	0.0338
0.1076	0.0439	0.1188	0.0324
0.1115	0.0430	0.1222	0.0314
0.1156	0.0418	0.1256	0.0303
-0.000214		-0.000317	

### pH Standardization in Seawater

In an attempt to estimate the magnitude of liquid-junction errors inherent in pH measurement in seawater of varying salinity, measurements in a cell with liquid junction have been carried out in buffered artificial seawater at salinities of 30, 35, and 45<sup>0</sup>/00, each containing Tris buffer at molalities of 0.02, 0.04, and 0.06.

The results of these measurements were treated in two ways, using the operational definition of pH (equation 3.16). First, values of  $p_{m_H}(X)$  were calculated where  $E_S$  and  $p_{m_H}(S)$  referred to the 35<sup>0</sup>/00 = S, 0.04m Tris solution. Values of  $p_{m_H}(S)$  were obtained from Ramette et al.<sup>34</sup> In the second case,  $pH_{NBS}$  was calculated by referencing  $E_X$  to the  $E_S$  and  $pH(S)$  values for the NBS 1:3.5 phosphate buffer. The results from these measurements and calculations are given in Table 4.

### pH Standardization in Clinical Media

Attempts to establish a primary reference standard for the measurement of pH near 7.4 at an ionic strength of 0.16, corresponding to blood plasma and other clinical media, have met with difficulty. Ideally, one would like to have a standard with pH at or near that of the sample. Furthermore, the ionic strength of the standard should match that of the sample. Although buffers have been proposed which meet these requirements,<sup>41,68</sup> they have been shown to be inconsistent with the NBS primary scale, that is, the pH values assigned based on measurements in cells without liquid

Table 4. Comparison of  $\text{p}m_{\text{H}}(\text{X})$  and  $\text{p}H_{\text{NBS}}$  Obtained by EMF Measurements of the Cell  $\text{Hg}; \text{Hg}_2\text{Cl}_2, 3.5\text{m KCl} || \text{Soln. S or X} | \text{H}_2 (\text{g}, 1\text{atm}); \text{Pt}$  at  $25^\circ \text{C}$  With Corresponding  $\text{p}m_{\text{H}}(\text{S})$  Values.

<u>Soln. X or S</u>	<u>S(<sup>0</sup>/00)</u>	<u>-E(V)</u>	<u><math>\text{p}m_{\text{H}}(\text{X})</math></u>	<u><math>\text{p}H_{\text{NBS}}</math></u>	<u><math>\text{p}m_{\text{H}}(\text{S})^{34}</math></u>
sw + 0.02m Tris	30	0.73473	8.190	8.198	8.185
sw + 0.04m Tris	30	0.73506	8.195	8.203	8.185
sw + 0.06m Tris	30	0.73494	8.193	8.202	8.187
sw + 0.02m Tris	35	0.73515	8.197	8.205	8.198
sw + 0.04m Tris	35	0.73538	8.201	8.209	8.201
sw + 0.06m Tris	35	0.73522	8.198	8.206	8.201
sw + 0.02m Tris	40	0.73552	8.203	8.211	8.216
sw + 0.04m Tris	40	0.73563	8.205	8.213	8.217
sw + 0.06m Tris	40	0.73563	8.205	8.213	8.220
1:3.5 Phosphate	I = 0.1m	0.68841	(pH(S) = 7.415)		

junction do not agree with the pH values determined by measurements in cells with liquid junction and the operational definition (equation 3.7). Pursuant to this problem, extensive measurements involving the buffers of TES, HEPES, and Tris have been carried out in conjunction with the NBS 1:3.5 phosphate "blood buffer" in an effort to reveal the causes of the discrepancies.<sup>43</sup> Factors investigated were a) the possible failure of the convention for  $\log \gamma_{\text{Cl}}$  at ionic strengths above 0.1m, and b) the appreciable residual liquid-junction potential when the relatively dilute NBS reference solutions are replaced by buffers at  $I = 0.16\text{m}$ .

Measurements have been made in cells without liquid junction to determine the EMF for solutions of the NBS phosphate "blood buffer" containing 0.01, 0.02, 0.04, and 0.06 mol kg<sup>-1</sup> NaCl as an independent check on the value of pH(S). The solution with the highest concentration of NaCl (0.06m) corresponds to an ionic strength of 0.16 mol kg<sup>-1</sup>. Figure 3 is a plot of  $p(a_{\text{H}}\gamma_{\text{Cl}})$  from equation 3.4 as a function of molality of NaCl added at 25 and 37°C. The intercepts,  $p(a_{\text{H}}\gamma_{\text{Cl}})^{\circ}$  at  $m_{\text{Cl}} = 0$ , found by linear regression analysis, were 7.520 and 7.499 at 25 and 37°C, respectively, with a mean deviation slightly greater than 0.001. Introduction of the pH convention to equation 3.5 gave values of pH(S) of 7.411 and 7.387 at the two temperatures; these compare well with the NBS assigned values. Table 5 gives the results of these and similar measurements involving the TES,

HEPES, and Tris buffers and the phosphate buffer, where its contribution to the total ionic strength was varied by adjusting the phosphate-NaCl ratio. All solutions contained enough NaCl to bring the ionic strength to  $0.16 \text{ mol kg}^{-1}$ . Assuming the pH convention is valid at this ionic strength (above its intended limit of  $0.1 \text{ m}$ ), pH(S) values were assigned to these buffer solutions based on equation 3.4. They are listed in Table 5 with the corresponding EMF's and temperatures.

Measurements in a cell with liquid junction have been carried out on the same solutions, and these results are listed in Table 6. The pH values listed here were calculated from the EMF values and equation 3.7, referenced to the EMF of the dilute phosphate buffer and its assigned pH(S) value. The values of pH(X) calculated in this manner differ appreciably from those assigned by the conventional approach. Both sets of values are summarized for the TES, HEPES, and Tris buffers in the second and last columns of Table 7. It is discrepancies of this sort that have led others<sup>29,69</sup> to postulate that a residual liquid-junction potential exists between dilute and higher ionic strength buffers when measured in cells with liquid junction.



Figure 3. Plot of  $p(a_{H^+}^{Cl})$  for the NBS phosphate "blood buffer" as a function of molality of added NaCl

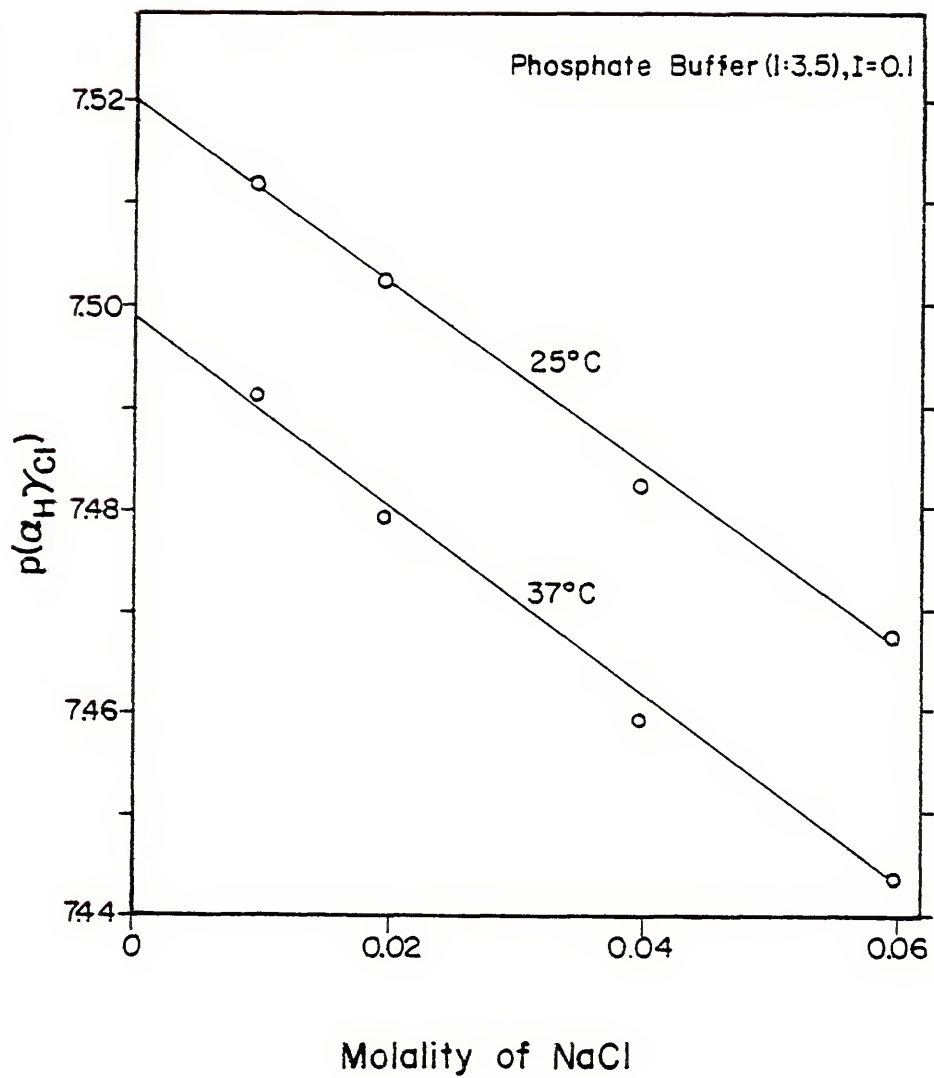


Table 5. Electromotive Force of Cells of Type 2.7: Pt; H<sub>2</sub>(g, 1atm)|Buffer Soln. |  
AgCl; Ag, at 25 and 37°C, in Volts

buffer, ionic strength, I	NaCl, I	E <sub>25</sub>	pH(S), 25°C	E <sub>37</sub>	pH(S), 37°C
phosphate 0.1	0.02	0.76675	7.385	0.77917	7.360
phosphate 0.1	0.04	0.74775	7.360	0.75945	7.334
phosphate 0.1	0.06	0.73644	7.339	0.74768	7.314
phosphate 0.08	0.08	0.72860	7.331	0.73950	7.306
phosphate 0.06	0.10	0.72232	7.323	0.73295	7.297
phosphate 0.04	0.12	0.71723	7.315	0.72769	7.290
0.02 TES	0.12	0.74340	7.758	0.74276	7.535
0.04 NaTES					
0.04 TES	0.12	0.72560	7.457	0.72429	7.235
0.04 NaTES					
0.02 HEPES	0.12	0.74619	7.805	0.75051	7.661
0.04 NaHEPES					
0.05 Tris-HCl	0.11	0.73529	7.746	0.72849	7.427
0.01667 Tris					

$$E^{\circ} = 0.22242$$

$$E^{\circ} = 0.21440$$

Table 6. Electromotive Force of Cells of Type 3.6: Hg; Hg<sub>2</sub>Cl<sub>2</sub>, 3.5M KCl|| Buffer Soln. |H<sub>2</sub> (g, latm); Pt, at 25 and 37°C, in Volts

buffer, ionic strength, I	NaCl, I	-E <sub>25</sub>	pH, 25°C	-E <sub>37</sub>	pH, 37°C
phosphate 0.1 <sup>a</sup>	0	0.6885	(7.411) <sup>b</sup>	0.6999	(7.387) <sup>b</sup>
phosphate 0.1	0.02	-	-	0.69779	7.353
phosphate 0.1	0.04	-	-	0.69588	7.322
phosphate 0.1	0.06	0.68242	7.308	0.69397	7.291
phosphate 0.08	0.08	0.68159	7.294	0.69324	7.279
phosphate 0.06	0.10	0.68082	7.281	0.69250	7.267
phosphate 0.04	0.12	0.67988	7.265	0.69151	7.251
0.02 TES	0.12	0.70644	7.714	0.70702	7.503
0.04 NaTES					
0.04 TES	0.12	0.68869	7.414	0.68862	7.204
0.04 NaTES					
0.02 HEPES	0.12	0.70939	7.764	0.71490	7.631
0.04 NaHEPES					
0.05 Tris-HCl	0.11	0.70472	7.685	0.69951	7.381
0.1667 Tris					

<sup>a</sup> Each phosphate buffer was composed of KH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> in the mole ratio 1:3.5.

<sup>b</sup> Reference values.

Table 7. Operational pH Values Calculated by Equation 3.7 from the EMF of Cell 3.6 vs. Phosphate-Chloride Standard Reference Solutions at 25 and 37°C

buffer solution	standard reference solution							
	25°C				37°C			
	NBS 0.1P <sup>a</sup>	0.1P + 0.02NaCl	0.1P + 0.04NaCl	0.1P + 0.06NaCl	0.1P + 0.08NaCl	0.08P + 0.10NaCl	0.06P + 0.10NaCl	
0.02 TES, 0.04 NaTES, 0.12 NaCl	7.714	-	-	7.745	7.751	7.756		
0.04 TES, 0.04 NaTES, 0.12 NaCl	7.414	-	-	7.445	7.451	7.456		
0.02 HEPES, 0.04 NaHEPES, 0.12 NaCl	7.764	-	-	7.795	7.801	7.806		
0.05 Tris-HCl, 0.01667 Tris, 0.11 NaCl	7.685	-	-	7.716	7.722	7.727		
0.02 TES, 0.04 NaTES, 0.12 NaCl	7.503	7.510	7.515	7.526	7.530	7.533		
0.04 TES, 0.04 NaTES, 0.12 NaCl	7.204	7.211	7.216	7.227	7.231	7.234		
0.02 HEPES, 0.04 NaHEPES, 0.12 NaCl	7.631	7.638	7.643	7.654	7.658	7.661		
0.05 Tris-HCl, 0.01667 Tris, 0.11 NaCl	7.381	7.388	7.393	7.404	7.408	7.411		

<sup>a</sup> p = Phosphate buffer (1:3.5); the numbers indicate the respective contributions of phosphate buffer and NaCl to the total ionic strength.

Table 7 - extended

<u>0.04P + 0.12NaCl</u>	<u>pH(S)</u>
7.764	7.758
7.464	7.457
7.814	7.805
7.735	7.746
7.542	7.535
7.243	7.235
7.670	7.661
7.420	7.427

## Isopiestic Measurements

### NaCl-SrCl<sub>2</sub> Mixtures

Of the aqueous systems MX-NX<sub>2</sub>, where M = Na, K, and N = Mg, Ca, Sr, Ba, only the system NaCl-SrCl<sub>2</sub> has not been studied by the isopiestic technique. Thermodynamic properties of this system are of interest to the chemical oceanographer, since both components are present in seawater.

The literature values<sup>4</sup> for the osmotic coefficients of strontium chloride in water are based upon the results of two isopiestic studies, one using KCl<sup>70</sup> and the other CaCl<sub>2</sub><sup>71</sup> as isopiestic reference. Downes<sup>72</sup> has drawn attention to the poor agreement between values derived from these studies and has made measurements using KCl as a reference. Measurements have been made in this laboratory<sup>73</sup> using NaCl as a reference up to about 3 mol kg<sup>-1</sup>; these are in excellent agreement with Downes' results. Comparison of the literature values with those from the present study are given in Table 8.

Data for the single electrolytes, NaCl and SrCl<sub>2</sub>, have been fitted to equations 4.6 and 4.8, and the best-fit parameters have been obtained.<sup>74</sup> These parameters, listed in Table 9, were used in fitting the data on the mixtures. The compositions of the mixtures in isopiestic equilibrium are given in Table 10, along with the molalities of the NaCl

reference solutions, and the osmotic coefficients calculated from equation 4.3. Osmotic coefficients for the NaCl reference solutions were obtained from the tables of Robinson and Stokes.<sup>4</sup>

The osmotic coefficients of the mixtures were fitted to the Scatchard neutral-electrolyte treatment (equation 4.11); the best-fit parameters and standard deviations  $\sigma(\phi)$  are given in Table 11. The computer program allows the inclusion of any or all parameters at the choice of the operator. This enables one to see the significance each parameter has on the standard deviation of fit.

The same procedure has been applied to the Pitzer treatment (equation 4.12), and the results are given in Table 11. It can readily be seen that the Pitzer treatment for the single electrolytes is far superior to that of Scatchard, in that these equations alone fit the data for the mixtures with a standard deviation  $\sigma(\phi) = 0.002$  without the inclusion of any mixing parameters, while the Scatchard treatment requires at least one mixing parameter.

#### NaCl-Na<sub>2</sub>CO<sub>3</sub> Mixtures

The carbonate system in seawater is important from the standpoint of acid-base processes which influence the pH and buffering capacity of this medium as well as the solubility of marine carbonates. It is of interest to investigate the



mixtures  $\text{NaCl-Na}_2\text{CO}_3$  at various compositions and ionic strengths to elucidate osmotic coefficient behavior and obtain thermodynamic information based on interactions of these electrolytes.

Data for the single electrolytes have been obtained,<sup>75</sup> and the useful parameters for treatment of the mixtures are given in Table 12 along with the standard deviations of fit. The isopiestic molalities and osmotic coefficients of the mixtures are listed in Table 13. Blanks in the table are where data were not included due to poor precision between duplicate cups. Results of fitting the mixtures to the Scatchard and Pitzer treatments are given in Table 14.

Table 8. Osmotic Coefficients in Aqueous  $\text{SrCl}_2$  Solutions at 25°C; Comparison of Results

$m_{\text{SrCl}_2}$	$\phi$ (KCl ref.) <sup>70</sup>	$\phi$ ( $\text{CaCl}_2$ ref.) <sup>71</sup>	$\phi$ <sup>4</sup>	$\phi$ (NaCl ref.) <sup>a</sup>
0.1	0.8494	0.8490	0.850	0.8487
0.2	0.8491	0.8514	0.854	0.8501
0.3	0.8590	0.8636	0.864	0.8615
0.4	0.8734	0.8797	0.880	0.8768
0.5	0.8906	0.8979	0.899	0.8946
0.6	0.9097	0.9177	0.918	0.9140
0.7	0.9303	0.9388	0.937	0.9349
0.8	0.9520	0.9611	0.959	0.9570
0.9	0.9746	0.9843	0.983	0.9802
1.0	0.9978	1.0086	1.009	1.0045
1.2	1.0460	1.0598	1.061	1.0558
1.4	1.0953	1.1144	1.116	1.1104
1.6	1.1460	1.1718	1.173	1.1674
1.8	1.1982	1.2320	1.232	1.2281
2.0	1.2530	1.2944	1.292	1.2905
2.5		1.4585	1.454	1.4551
3.0		1.6294	1.631	1.6300
3.5		1.8009	1.802	1.8010
4.0		1.9669	1.966	1.9669
4.2		2.0302		2.0302

<sup>a</sup> Present work.

Table 9. Parameters for Eqs. 4.6 and 4.8 Used in the Treatment of  $\text{NaCl-SrCl}_2\text{-H}_2\text{O}$  Mixtures

Parameters for Eq. 4.6  
 $S = -1.17202$

	$\text{NaCl}^a$	$\text{SrCl}_2^b$
A	1.4635	1.6011
B	0.041340	0.031312
C	0.020830	0.0095259
D	-0.0016130	-0.00051960
E	0.000043460	0.000013640
I(max.)	6.0	9.0
$\sigma(\phi)$	0.0004	0.0012

Parameters for Eq. 4.8  
 $A^\phi = -0.392$

	$\text{NaCl}^c$	$\text{SrCl}_2^b$
$\beta(0)$	0.07669	0.28994
$\beta(1)$	0.26461	1.5795
$C^\phi$	0.0012193	-0.003755
I(max.)	6.0	6.0
$\sigma(\phi)$	0.0007	0.0017

<sup>a</sup> Parameters taken from ref. 74.

<sup>b</sup> Combined fit to results of ref. 72 and present work (Table 8).

<sup>c</sup> Parameters obtained by fitting smoothed values of  $\phi_{\text{NaCl}}$  from ref. 4.

Table 10. Compositions and (Osmotic Coefficients) of Isopiestic Solutions in the System  $\text{NaCl(A)} - \text{SrCl}_2\text{(B)} - \text{H}_2\text{O}$

$y_B = 0.0$	<u>0.1722</u>	<u>0.3528</u>	<u>0.5259</u>	<u>0.6717</u>	<u>0.8291</u>
I = 0.6035	0.6633(0.9189)	0.7419(0.9119)	0.8336(0.9067)	0.9320(0.8999)	1.0671(0.8917)
0.9757	1.0698(0.9328)	1.1890(0.9313)	1.3299(0.9304)	1.4784(0.9288)	1.6788(0.9279)
1.4578	1.5915(0.9565)	1.7586(0.9605)	1.9543(0.9658)	2.1577(0.9708)	2.4283(0.9786)
2.0146	2.1882(0.9914)	2.4037(1.0015)	2.6563(1.0127)	2.9115(1.0254)	3.2476(1.0428)
2.4670	2.6716(1.0215)	2.9217(1.0365)	3.2127(1.0533)	3.5052(1.0714)	3.8872(1.0959)
3.7057	2.9231(1.0392)	3.1938(1.0554)	3.5033(1.0752)	3.8141(1.0959)	4.2170(1.1245)
3.0150	3.2524(1.0613)	3.5442(1.0807)	3.8774(1.1039)	4.2092(1.1285)	4.6382(1.1617)
3.3386	3.5934(1.0860)	3.9076(1.1082)	4.2646(1.1347)	4.6174(1.1630)	5.0699(1.2016)
3.6711	3.9453(1.1117)	4.2820(1.1366)	4.6630(1.1663)	5.0355(1.1986)	5.5097(1.2427)
4.0015	4.2946(1.1377)	4.6517(1.1655)	5.0533(1.1989)	5.4447(1.2349)	5.9396(1.2841)

Table 11. Best-Fit Mixing Parameters for the System  
 $\text{NaCl(A)} - \text{SrCl}_2\text{(B)} - \text{H}_2\text{O}$

1. Scatchard neutral-electrolyte treatment					
$b_{01}$	$b_{02}$	$b_{03}$	$b_{12}$	$b_{13}$	$\sigma(\phi)$
-	-	-	-	-	0.0050
0.0096	-	-	-	-	0.0017
0.0212	-0.0027 <sub>4</sub>	-	-	-	0.0011
0.0235	-0.0040 <sub>2</sub>	0.0001 <sub>6</sub>	-	-	0.0011
0.0243	-0.0038	-	-0.0014	-	0.0005
0.0178	0.0002 <sub>3</sub>	-0.0005 <sub>4</sub>	-0.0003 <sub>7</sub>	-0.0002 <sub>7</sub>	0.0005
2. Pitzer treatment					
$\theta_{\text{Na,Sr}}$	$\theta_{\text{Na,Sr}}$	$\psi_{\text{Na,Sr,Cl}}$	$\sigma(\phi)$		
-	-	-	0.0021		
0.0036	-	-	0.0017		
-0.0096	0.0031	-	0.0014		
-0.0084	-	0.0036	0.0015		
-0.0076	0.0068	-0.0052	0.0013		

Table 12. Parameters for Eq. 4.6 and 4.8 Used in the Treatment of  $\text{NaCl}-\text{Na}_2\text{CO}_3-\text{H}_2\text{O}$  Mixtures

Parameters for Eq. 4.6

$$S = -1.17202$$

	$\text{NaCl}^a$	$\text{Na}_2\text{CO}_3^b$
A	1.4635	1.4226
B	0.041340	-0.065322
C	0.020830	0.0084332
D	-0.0016130	-0.00028700
E	0.000043460	0.0000018700
I(max)	6.0	9.0
$\sigma(\phi)$	0.0004	0.0020

Parameters for Eq. 4.8

$$A^\phi = -0.392$$

	$\text{NaCl}^c$	$\text{Na}_2\text{CO}_3^d$
$\beta(0)$	0.076690	0.040822
$\beta(1)$	0.026461	1.4679
$C^\phi$	0.0012193	0.0042374
I(max)	6.0	9.0
$\sigma(\phi)$	0.0007	0.0020

<sup>a</sup> Parameters taken from ref. 74.

<sup>b</sup> Parameters obtained by fitting smoothed values of  $\phi_{\text{Na}_2\text{CO}_3}$  from ref. 75.

<sup>c</sup> Parameters obtained by fitting smoothed values of  $\phi_{\text{NaCl}}$  from ref. 4.

<sup>d</sup> Parameters taken from ref. 75.

Table 13. Compositions and (Osmotic Coefficients) of Isopiestic Solutions in the System  $\text{NaCl(A)} - \text{Na}_2\text{CO}_3(\text{B}) - \text{H}_2\text{O}$

$y_{\text{B}} = 0.0$	<u>0.1713</u>	<u>0.3500</u>	<u>0.5371</u>	<u>0.6996</u>	<u>0.8518</u>
I = 0.2936	0.3223(0.9182)	0.3656(0.8971)	0.4273(0.8659)	0.4978(0.8362)	0.5872(0.8028)
0.3981	-	0.4983(0.8912)	0.5845(0.8570)	0.6837(0.8243)	0.8111(0.7868)
0.9292	1.0470(0.9056)	1.2002(0.8756)	1.4192(0.8351)	1.6915(0.7883)	2.0590(0.7334)
1.3451	1.5113(0.9238)	1.7404(0.8890)	2.0716(0.8424)	-	3.0705(0.7242)
2.0026	2.2562(0.9547)	2.6073(0.9156)	3.1197(0.8631)	-	4.6840(0.7324)
2.0985	2.3657(0.9594)	2.7338(0.9202)	3.2708(0.8675)	3.9464(0.8083) <sup>a</sup>	4.9021(0.7357) <sup>b</sup>
2.3039	2.5986(0.9706)	3.0031(0.9308)	3.5942(0.8772)	4.3412(0.8166) <sup>a</sup>	5.3943(0.7429) <sup>b</sup>
2.4158	2.7270(0.9764)	3.1576(0.9346)	3.7852(0.8793)	4.5809(0.8174)	5.6896(0.7454)

<sup>a</sup>  $y_{\text{B}}$  is actually 0.6988.

<sup>b</sup>  $y_{\text{B}}$  is actually 0.8490.

Table 14. Best-Fit Mixing Parameters for the System  
 $\text{NaCl(A)} - \text{Na}_2\text{CO}_3\text{(B)} - \text{H}_2\text{O}$

1. Scatchard neutral-electrolyte treatment					
$b_{01}$	$b_{02}$	$b_{03}$	$b_{12}$	$b_{13}$	$\sigma(\phi)$
-	-	-	-	-	0.047
-0.1099	-	-	-	-	0.0081
-0.0956 <sub>2</sub>	-0.0036 <sub>6</sub>	-	-	-	0.0081
-0.174 <sub>4</sub>	0.0424 <sub>0</sub>	-0.0061 <sub>9</sub>	-	-	0.0073
-0.165 <sub>4</sub>	0.0197 <sub>1</sub>	-	0.0180 <sub>2</sub>	-	0.0047
-0.136 <sub>4</sub>	-0.0243 <sub>8</sub>	0.00392 <sub>1</sub>	0.0147 <sub>8</sub>	0.00172 <sub>3</sub>	0.0047
2. Pitzer treatment					
$\theta_{\text{Na, Sr}}$	$\theta_{\text{Na, Sr}}$	$\psi_{\text{Na, Sr, Cl}}$	$\sigma(\phi)$		
-	-	-	0.030		
-0.0495 <sub>8</sub>	-	-	0.012		
-0.0898 <sub>1</sub>	0.0103 <sub>1</sub>	-	0.010		
-0.1605	-	0.0503 <sub>0</sub>	0.0047		
-0.1607	-0.00254 <sub>4</sub>	0.0548 <sub>8</sub>	0.0047		



## CHAPTER 7 DISCUSSION

### Electromotive Force Measurements

#### Activity Coefficient of HCl in Seawater

For the  $\text{HCl-MgCl}_2$  system, two values of the Harned slope,  $\alpha$ , at  $I = 0.1 \text{ mol kg}^{-1}$  and  $25^\circ\text{C}$  have been reported previously. That of Downes,<sup>76</sup> based on measurements made by Smith,<sup>77</sup> is 0.0521, while Khoo et al.<sup>78</sup> found  $\alpha = 0.0326$ . This is a rather large discrepancy. The value obtained from this work,  $\alpha = 0.0493$ , tends to support the value reported by Downes.

The primary purpose of this study was to derive values of  $\alpha$  at ionic strengths corresponding to those of seawater of salinities 20, 35, and  $45^0/00$ , and thus to elucidate the behavior of activity coefficients in solutions resembling seawater. It is also of interest to evaluate the trace activity coefficient of HCl in the mixtures and compare it to earlier measurements. This has been done in two ways. First, values of  $\alpha$  obtained from the present work involving  $\text{HCl-MgCl}_2$  (Table 3) were combined with those of an earlier study of  $\text{HCl-NaCl}$ , weighting the two in accord with the relative contributions of the two salts

to the total ionic strength of a seawater solution containing only those two salts (equation 2.40). In another approach,  $\gamma_{\text{HCl}}^{\text{tr}}$  was calculated from the Harned slope obtained from HCl-NaCl-MgCl<sub>2</sub> mixtures at  $I = 0.6729$  (Table 3), treating NaCl + MgCl<sub>2</sub> as one component (equation 2.38), where  $y$  is the ionic strength contribution of the two salts to the total ionic strength. In Table 15, the values of  $\gamma_{\text{HCl}}^{\text{tr}}$  obtained in these two ways are compared with the values obtained by Khoo *et al.* from EMF measurements of 0.01m HCl in synthetic seawater. Although sulfate was omitted, the salt mixture used in the latter study approached closely the composition of natural seawater, being composed of NaCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, and KCl in the correct proportions. An examination of the table shows that  $\gamma_{\text{HCl}}^{\text{tr}}$  derived from the Harned rule, using  $\alpha$  measured for HCl in the salt mixture composed of both NaCl and MgCl<sub>2</sub>, agrees well with that calculated by equation 2.40 from the individual values of  $\alpha$  from the HCl-NaCl and HCl-MgCl<sub>2</sub> systems. Furthermore, it is evident that  $\gamma_{\text{HCl}}^{\text{tr}}$  is nearly the same in a mixture of the two salts as in a mixture of the same ionic strength but containing the four salts predominant in seawater. The average difference at the nine temperatures is less than 0.001; for a solution of NaCl alone ( $I = 0.6729 \text{ mol kg}^{-1}$ ),  $\gamma_{\text{HCl}}^{\text{tr}}$  differs from that in seawater on the average by about 0.006. Thus, the drop in  $\gamma_{\text{HCl}}$  from pure HCl to seawater is accounted for by the effect of the two major salts, NaCl and MgCl<sub>2</sub>.

Table 15. Comparison of the Trace Activity Coefficient of HCl ( $\gamma_A^{tr}$ ) in NaCl-MgCl<sub>2</sub> Mixtures With That Determined Experimentally in Synthetic Seawater (sw)

t, °C	I = 0.3809 (S = 20 <sup>0</sup> /00)		I = 0.6729 (S = 35 <sup>0</sup> /00)		I = 0.8720 (S = 45 <sup>0</sup> /00)		sw
	Eq. 2.40 <sup>a</sup>	sw <sup>b</sup>	Eq. 2.40	Eq. 2.38 <sup>c</sup>	sw	Eq. 2.40	
5	0.740	0.740	0.741	0.741	0.741	0.752	0.752
10	0.738	0.738	0.739	0.739	0.738	0.747	0.748
15	0.739	0.739	0.736	0.736	0.735	0.747	0.745
20	0.733	0.737	0.734	0.733	0.732	0.744	0.741
25	0.730	0.733	0.730	0.730	0.729	0.739	0.738
30	0.727	0.730	0.726	0.727	0.725	0.737	0.734
35	0.725	0.728	0.722	0.723	0.722	0.731	0.730
40	0.722	0.726	0.718	0.719	0.718	0.726	0.726
45	0.718	0.722	0.713	0.714	0.714	0.722	0.722

<sup>a</sup> Calculated by Eq. 2.40 from  $\alpha$  values for HCl-NaCl mixtures (reference 24) and for HCl-MgCl<sub>2</sub> mixtures (present work).

<sup>b</sup> From experimental data, reference 25.

<sup>c</sup> Calculated by Eq. 2.38 from  $\alpha$  for HCl-NaCl-MgCl<sub>2</sub> mixtures,  $\gamma_{NaCl/MgCl_2} = 1$ .

In this respect, it is of interest to consider the results in light of Pitzer's recent treatment concerning electrolyte mixtures. The data for HCl in mixtures of NaCl and  $\text{MgCl}_2$  have been fitted to the Pitzer equation (equation 4.12) in an attempt to estimate the pertinent mixing terms. The parameters  $\beta_{\text{MX}}^{(0)}$  and  $\beta_{\text{MX}}^{(1)}$  for the single electrolytes were taken from Pitzer's tabulated values.<sup>48</sup> Strictly, the  $C_{\text{MX}}^\phi$  terms should have been included. However, they were unavailable and were taken to be zero. The best-fit values of interaction terms  $\Theta_{\text{MN}}$ ,  $\Theta'_{\text{MN}}$ , and  $\psi_{\text{MNX}}$  were derived by curve-fitting. The results are summarized in Table 16. It is evident from the standard deviations given in the last column that the properties of the mixtures are not well accommodated by  $\beta^{(0)}$  and  $\beta^{(1)}$  for the individual electrolytes alone. Inclusion of the cation-cation mixing term,  $\Theta$ , produces considerable improvement. The parameter,  $\Theta'$ , which represents a dependence of  $\Theta$  on ionic strength, appears to be of little importance in fitting the data. The ternary interaction term,  $\psi$ , produces some improvement; however, its inclusion would result in a term quadratic in  $y_{\text{MgCl}_2}$  in Pitzer's equation for the activity coefficients in the mixture. Since the data obey Harned's rule without such a term, the necessity of  $\psi$  is questionable.

The Harned slope appears to be linearly dependent on temperature, as shown by the slope  $da/dT$  given at the foot of Table 15. Since  $-\alpha y_{\text{B}} I = \log (\gamma_{\text{HCl}}/\gamma_{\text{HCl}}^\circ)$ , the quantity

Table 16. Mixing Parameters (Pitzer Treatment) for the  
System  $\text{HCl-MgCl}_2\text{-H}_2\text{O}$

$\theta_{\text{H,Mg}}$	$\theta'_{\text{H,Mg}}$	$\psi_{\text{H,Mg,Cl}}$	$\frac{10^3 s}{\text{s}}^a$
-	-	-	30.9
-0.2904	-	-	5.8
-0.3430	0.2728	-	4.1
-0.4357	-	0.3843	2.9
-0.4651	-0.1401	0.5337	2.8

<sup>a</sup> Standard deviation of  $\log \gamma_A$ .

$d\alpha/dT$  may be related to the difference in partial molal heat content of HCl in its pure solution and in a mixture with  $MgCl_2$  by the equation:

$$\begin{aligned} -4.606RT^2 y_B I (d\alpha/dT) &= 2RT^2 \frac{d}{dT} \ln (\gamma_{HCl}/\gamma_{HCl}^\circ) \\ &= \bar{L}_{HCl}(y_{MgCl_2} = 0) - \bar{L}_{HCl}(y_{MgCl_2}) \end{aligned} \quad (7.1)$$

Thus, the partial molal enthalpy appears to be linearly dependent on  $y_B$ , and in this respect an analog of Harned's rule exists, at least for  $5^\circ C < T < 45^\circ C$  and  $0.1 < I < 0.9$ .

#### pH Standardization in Seawater

Comparison of results (Table 4) for  $pm_H(X)$  obtained by the operational definition with  $pm_H(S)$  values calculated from equation 3.15 shows that a discrepancy does exist when salinity is varied. At a salinity of 30<sup>0</sup>/00, for example, this amounts to an average of 0.007 pH unit higher for the  $pm_H(X)$  values, while at  $S = 40^0/00$ , the operational values are, on the average, 0.013 pH unit lower than the corresponding  $pm_H(S)$  values. Within a given salinity, however,  $pm_H(X)$  values are essentially identical regardless of the Tris buffer concentration, indicating a stabilization of the residual liquid-junction potential by the seawater medium.

It is interesting to note that when the operational definition is employed using  $E_x$  with  $E_s$  and  $pH(S)$  of the NBS 1:3.5 phosphate buffer, the resulting  $pH_{NBS}$  values are very

close (0.007 pH unit on the average) to the corresponding  $\text{pm}_\text{H}(\text{S})$  values, even though there is a large difference in ionic strength between the seawater solutions and the dilute ( $I = 0.1\text{m}$ ) phosphate buffer.

Since  $\text{pH}(\text{X})$  differs from  $\text{pH}(\text{S})$  ( $= -\log m_\text{H}\gamma_\text{H}$ ) by the liquid-junction term,  $E_\text{j}/k$ , the relationship between  $\text{pH}_\text{NBS}$  and  $\text{pm}_\text{H}(\text{S})$  can be written as:

$$\text{pm}_\text{H}(\text{S}) = \text{pH}_\text{NBS} + \log \gamma_\text{H} + E_\text{j}/k \quad (7.2)$$

The close agreement between  $\text{pH}_\text{NBS}$  and  $\text{pm}_\text{H}(\text{S})$  must then be attributed to a cancellation of the liquid-junction potential and activity coefficient terms. Robinson and Bates have recently estimated  $\gamma_\text{Cl} = 0.639$  in seawater of 35<sup>0</sup>/00 salinity, based on an hydration number method developed earlier.<sup>67</sup> Using  $\gamma_\text{HCl}^\text{tr} = 0.729$  at 25°C, one obtains 0.832 for  $\gamma_\text{H}$  ( $= \gamma_\text{HCl}^2/\gamma_\text{Cl}$ ). Using this value in equation 7.2 with  $\text{pm}_\text{H}(\text{S}) - \text{pH}_\text{NBS} = -0.007$  at 35<sup>0</sup>/00 salinity, the residual liquid-junction potential is estimated to be about 4.3mV.

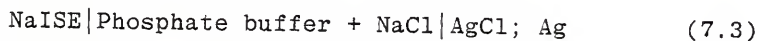
#### pH Standardization in Clinical Media

As pointed out in Chapter 6, discrepancies between column 2 and the last column of Table 7 are thought to arise as the result of an appreciable residual liquid-junction potential caused by the difference in ionic strength between the relatively dilute NBS phosphate "blood buffer" and the higher ionic strength ( $I = 0.16\text{m}$ ) Tris, HEPES, and TES buffers.

The pH(S) values obtained for the phosphate buffer + NaCl by measurements in a cell without liquid junction in all likelihood lie close to the NBS standard scale, based on the same pH convention. The reasoning is as follows.

Calculations from equation 3.3 for the logarithm of the activity coefficient of chloride ion at 25°C give -0.110 at  $I = 0.01m$  and -0.128 at  $I = 0.16m$ . These values are nearly the same as the logarithm of the mean activity coefficient ( $\log \gamma_{\pm}$ ) of NaCl at  $I = 0.1m$  (-0.109) and at  $I = 0.16m$  (-0.126). At 37°C,  $\log \gamma_{Cl}$  is -0.130 at  $I = 0.16m$ , while  $\log \gamma_{\pm}$  is -0.128. Furthermore, the hydration convention<sup>79</sup> yields -0.130 for  $\log \gamma_{Cl}$  in a solution of NaCl of molality  $0.16 \text{ mol kg}^{-1}$ .

One expects that  $\log \gamma_{\pm}$  and  $\log \gamma_{Cl}$  will vary linearly as phosphate is added to a solution of NaCl maintaining a constant ionic strength.<sup>5</sup> To estimate the magnitude of this change, the sodium glass electrode was employed in a cell of the type:



and the following EMF data were obtained:

<u>ionic strength</u>		<u>E(V)</u>	
<u>phosphate</u>	<u>NaCl</u>	<u>25°C</u>	<u>37°C</u>
0	0.16	0.0432	0.0465
0.04	0.12	0.0540	0.0574
0.10	0.06	0.0767	0.0814



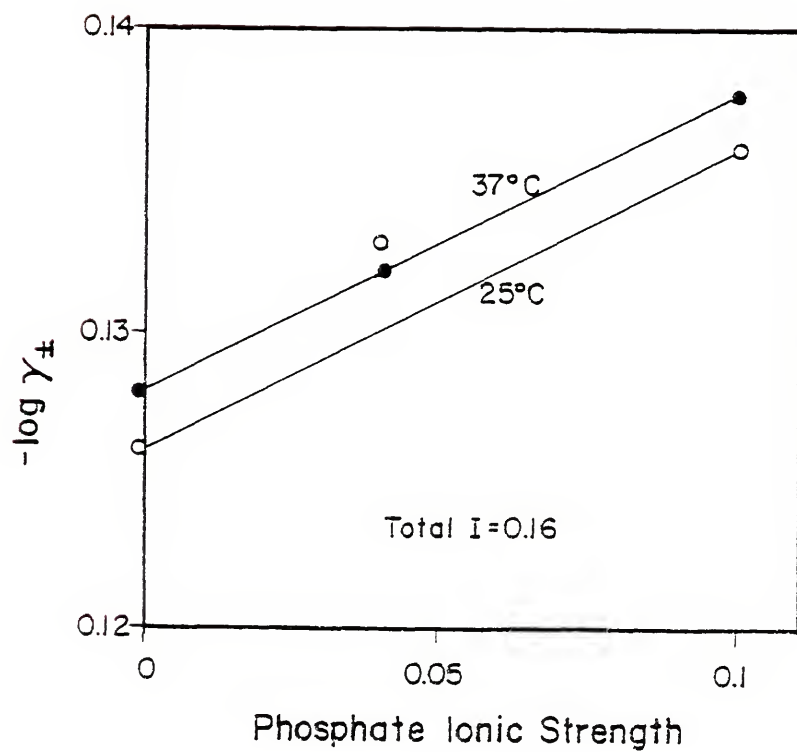
The standard potential of cell 7.3 was derived knowing  $\log \gamma_{\pm}$  in the 0.16m NaCl solution, and the activity coefficients in the mixtures were calculated by:

$$-\log \gamma_{\pm} = \frac{(E - E^{\circ})}{2k} + \frac{1}{2} \log (m_{\text{Na}} m_{\text{Cl}}) \quad (7.4)$$

The results, plotted in Figure 4, are not of high accuracy but do demonstrate a linear increase of  $-\log \gamma_{\pm}$  when NaCl is replaced by buffer. This increase amounts to only 0.001 in  $\log \gamma_{\pm}$  for each increment of 0.01 in the ionic strength contribution of phosphate. Therefore any discrepancy in calculation of  $-\log \gamma_{\text{Cl}}$  by the convention for a solution of phosphate ( $I = 0.06$ ) and NaCl ( $I = 0.1$ ) would not amount to more than 0.006, small when compared with the difference of 0.042 at 25°C and 0.030 at 37°C in pH values derived from cells with and without liquid junction (see Tables 5 and 6).

Having values of pH(S) for buffer solutions with NaCl (last column, Table 7) that appear to lie close to the NBS standard scale, it was possible to examine the effect of ionic strength and composition of the phosphate standard on the pH(X) values determined for the TES, HEPES, and Tris buffers from the cell with liquid junction. By taking values of  $E_s$  and pH(S) for the reference phosphate-NaCl solutions from Tables 6 and 5 respectively and the values of  $E_x$  for the other buffers (Table 6) and applying equation 3.7, the pH(X) values listed in Table 7 were calculated; each column heading being the reference buffer composition. The

Figure 4. Variation of the logarithm of the mean activity coefficient of NaCl in phosphate-chloride mixtures of  $I = 0.16m$ , as a function of composition at 25 and 37° C



results are shown graphically in Figure 5. The horizontal dotted lines indicate the values of pH(S) assigned to the respective buffers.

It is clear from Figure 5 that the greater part of the discrepancy between the operational pH(X) and the conventional activity pH(S) is removed simply by matching the ionic strength of the standard to that of the unknown sample. By increasing the NaCl molality further at the expense of phosphate such that  $I(\text{phosphate}) = 0.06\text{m}$  and  $I(\text{NaCl}) = 0.10\text{m}$ , the residual liquid-junction potential is completely eliminated for the TES and HEPES buffers although a difference of about 0.9mV (0.015 pH unit) persists for the Tris buffer.

Estimates of liquid-junction potentials at the junction buffer || 3.5M KCl have been made by use of the Henderson equation.<sup>33</sup> Using available limiting ionic conductances at 25°C and estimating those of  $\text{HPO}_4^{2-}$ ,  $\text{TES}^-$ ,  $\text{HEPES}^-$ , and  $\text{TrisH}^+$ , the following values have been obtained:

<u>buffer</u>	<u>I, m</u>	<u>Ej, mV</u>
1:3.5 phosphate	0.10	1.9
P(0.10) + NaCl(0.06)	0.16	1.5
P(0.08) + NaCl(0.08)	0.16	1.4
P(0.06) + NaCl(0.10)	0.16	1.3
P(0.04) + NaCl(0.12)	0.16	1.3
1:1 TES(0.04) + NaCl(0.12)	0.16	1.3
1:2 TES(0.04) + NaCl(0.12)	0.16	1.3
1:2 HEPES(0.04) + NaCl(0.12)	0.16	1.3
1:3 Tris(0.05) + NaCl(0.11)	0.16	0.8

It is evident that the residual liquid-junction potential when the blood buffer ( $I = 0.1\text{m}$ ) is replaced by a TES buffer ( $I = 0.16\text{m}$ ), for example, should not exceed 0.6mV (0.01 pH unit), whereas the observed differences are three times this

Figure 5. Effect of the ionic strength and composition of the reference standard on the operational pH values of TES, HEPES, and Tris buffer solutions of ionic strength 0.16m at 37° C

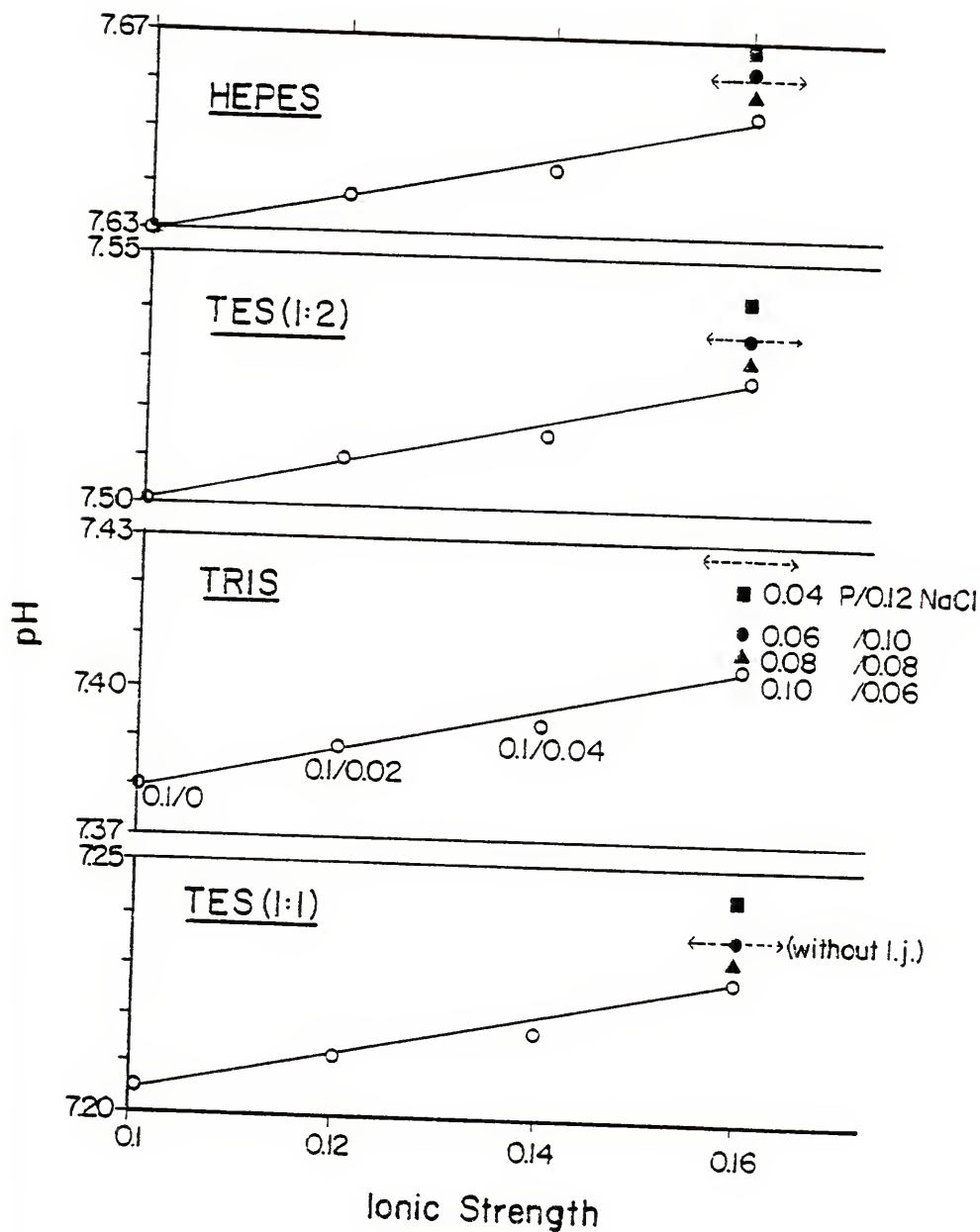


figure. However, the calculations do lead to the conclusion that the potential difference should be small when a buffer 0.06M in phosphate and 0.1M in NaCl is measured against the TES and HEPES buffers of the same ionic strength.

The low value of  $E_j$  calculated for the Tris + NaCl buffers compared with the other buffers of the same ionic strength is the result of a larger value of the difference in the limiting ionic conductances,  $\Sigma c_{-}\lambda_{-}^{\circ} - \Sigma c_{+}\lambda_{+}^{\circ}$ , which, in turn, is caused by the fact that the mobility of the  $\text{TrisH}^{+}$  cation is lower than those of  $\text{Na}^{+}$  and  $\text{K}^{+}$ , the cations of which the other buffers are composed. The three hydroxyl groups on the Tris structure and their capacity for hydrogen-bonding to water support this suggestion.

### Isopiestic Measurements

#### Scatchard Treatment

In the simplest case, the osmotic coefficient of a solution composed of 1:1 and a 1:2 or 2:1 electrolyte with a common ion will be a simple function of the contributions of single electrolyte properties as described by the truncated form of equation 4.11:

$$(1 + y_A)\phi_{\text{MIX}} = 2\phi_A^{\circ}y_A + \phi_B^{\circ}y_B \quad (7.5)$$

This type of behavior would be observed if only binary interactions between ions of opposite charge were present, as first postulated by Guggenheim.<sup>13</sup> In reality, however, particularly

at higher ionic strengths, it becomes necessary to consider binary interactions between like charged ions as well as additional higher order (e.g., ternary) interactions. This forces the inclusion of additional terms to equation 7.5 if one wishes to describe the data mathematically. Scatchard's general equation for the systems studied here may be written as:

$$(1 + y_A)\phi_{\text{MIX}} = 2\phi_A^0 y_A + \phi_B^0 y_B + y_A y_B \beta_0 + y_A y_B (y_A - y_B) \beta_1 \quad (7.6)$$

where  $\beta_0 = b_{01}I + b_{02}I^2 + b_{03}I^3 + \dots$  and  $\beta_1 = b_{12}I^2 + b_{13}I^3 + \dots$ . The functional dependence on  $m_A$  and  $m_B$  of the terms in which the mixing parameters,  $b_{ij}$ , reside has led Robinson<sup>80</sup> to identify each parameter with a particular type of ionic interaction, none of which is characteristic of only the single salt solutions. The  $b_{01}$  term is identified with binary interactions between ions of like charge,  $b_{02}$  with ternary interactions involving two like-charged ions and one of opposite charge, and  $b_{12}$  with ternary interactions among ions all of like-charge. The terms  $b_{03}$  and  $b_{13}$  are sometimes associated with quaternary interactions but are most likely only "data-fitting" parameters. The inclusion of any additional terms is superfluous. The Oak Ridge computer program used in this work<sup>81</sup> allows the evaluation of the first five parameters.

Examination of the top of Tables 11 and 14 shows that while the inclusion of all five of the above parameters gives the best fit to the experimental results, the same



agreement can be obtained using only  $b_{01}$ ,  $b_{02}$ , and  $b_{12}$ . The relative magnitude of the parameters between the NaCl-SrCl<sub>2</sub> and the NaCl-Na<sub>2</sub>CO<sub>3</sub> studies, as well as the inferior fit of the latter data, indicate much more complex behavior in the system involving carbonate. This is reinforced by a comparison of Figures 6 and 7, in which a plot of  $\phi_{\text{MIX}}$  as a function of  $I$  has been made for the two systems. It can readily be seen that due to the large difference in  $\phi^\circ$  for the pure solutions NaCl and Na<sub>2</sub>CO<sub>3</sub>,  $\phi_{\text{MIX}}$  is highly dependent on  $\gamma_{\text{Na}_2\text{CO}_3}$  at high ionic strength while this is not the case in the NaCl-SrCl<sub>2</sub> system.

The free energy of a solution of a single electrolyte is made up of the free energy of the components in their standard state and the ideal free energy which is a function of the concentration of solute. Any additional contribution is referred to as excess free energy and is made up of Debye-Hückel forces and any additional interaction terms. It is this excess free energy which is estimated by the activity and osmotic coefficients.

When two solutions are mixed, there arises an excess free energy of mixing above and beyond that present in each respective solution, and it is this quantity for which the interaction parameters may have some significance. It is of interest, therefore, to calculate this excess free energy of mixing for our two systems. From the last two terms on the

Figure 6. Plot of  $\phi_{\text{MIX}}$  as a function of ionic strength in the system  $\text{NaCl}(\text{A}) - \text{SrCl}_2(\text{B}) - \text{H}_2\text{O}$  for various ionic strength fractions,  $y_{\text{B}}$

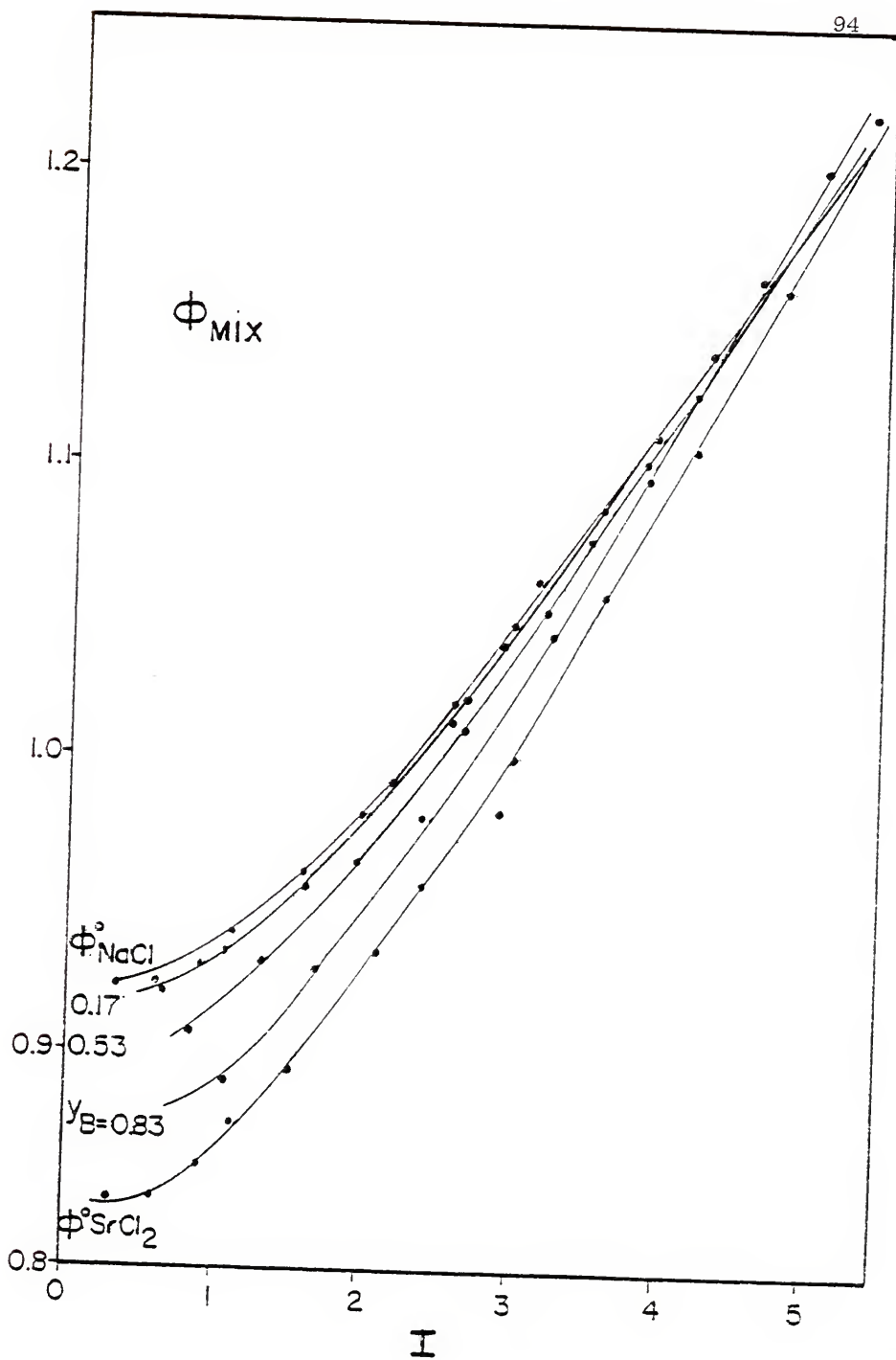
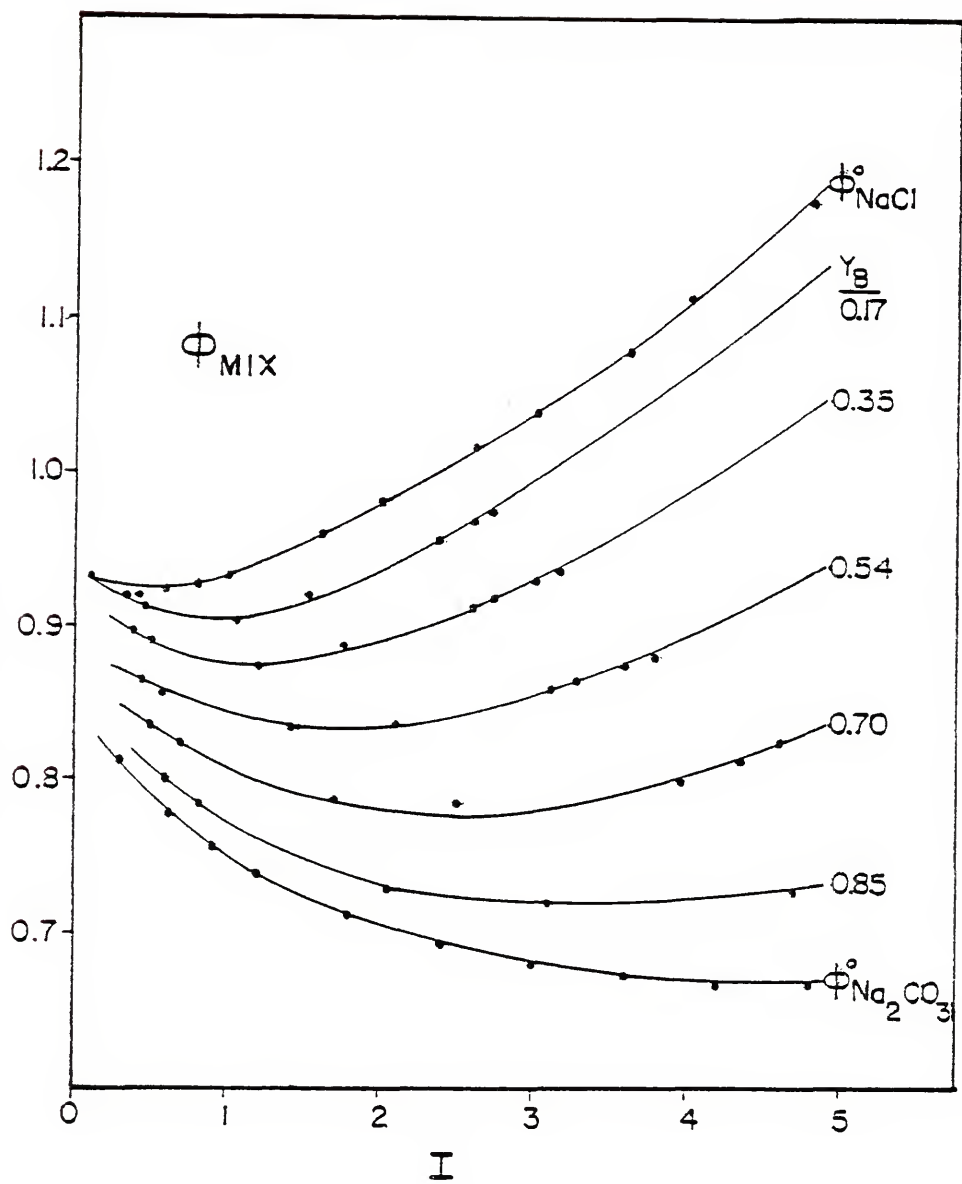


Figure 7. Plot of  $\phi_{\text{MIX}}$  as a function of ionic strength in the system  $\text{NaCl}(\text{A}) - \text{Na}_2\text{CO}_3(\text{B}) - \text{H}_2\text{O}$  for various ionic strength fractions,  $y_{\text{B}}$



right of equation 7.6, the excess free energy of mixing per kilogram of solvent at constant ionic strength may be given as:<sup>73</sup>

$$\Delta G_{\text{MIX}}^E = RTI y_A y_B [B_0 + B_1(y_A - y_B)] \quad (7.7)$$

where  $B_0 = b_{01}I + (1/2b_{02})I^2 + (1/3b_{03})I^3$  and  $B_1 = (1/2b_{12})I^2 + (1/3b_{13})I^3$ .

The  $\Delta G_{\text{MIX}}^E$  for each system has been calculated for the case  $y_A = y_B = 0.5$  at three ionic strengths using only the  $b_{01}$  and  $b_{02}$  values listed in Tables 11 and 14. The results for NaCl-SrCl<sub>2</sub> are listed in Table 17 with other members of the series for comparison. The NaCl-Na<sub>2</sub>CO<sub>3</sub> results are compared with the results of NaCl-Na<sub>2</sub>SO<sub>4</sub> from another study<sup>52</sup> (Table 17). It can be seen that there is a trend in  $\Delta G_{\text{MIX}}^E$  with atomic number within the alkaline-earth group, and that this quantity increases with ionic strength as expected. From the results of the NaCl-SrCl<sub>2</sub> system, it would appear that the relatively slight  $\Delta G_{\text{MIX}}^E$  is destabilizing or unfavorable due to the positive sign. This is accounted for solely by the  $b_{01}$  term and implies that a repulsive energy arises from new interactions between Na<sup>+</sup> and Sr<sup>++</sup> which are greater than the sum of Cl<sup>-</sup> - Cl<sup>-</sup>, Na<sup>+</sup> - Na<sup>+</sup>, and Sr<sup>+2</sup> - Sr<sup>+2</sup> repulsive energies that no doubt exist in the single electrolyte solutions. From the sign of the  $b_{02}$  and  $b_{12}$  terms, however, it appears that there is a net attractive energy gained among ternary interactions.

Table 17. Excess Free Energy of Mixing ( $\text{J kg}^{-1}$ );  
Comparison of Results

	I		
	1	3	5
$\text{NaCl} - \text{MgCl}_2 - \text{H}_2\text{O}^{55}$	35	250	578
$\text{NaCl} - \text{CaCl}_2 - \text{H}_2\text{O}^{74}$	17	130	318
$\text{NaCl} - \text{SrCl}_2 - \text{H}_2\text{O}$	12	95	222
$\text{NaCl} - \text{BaCl}_2 - \text{H}_2\text{O}^{81}$	16	46	-11
$\text{NaCl} - \text{Na}_2\text{CO}_3$	-96	-758	-1799
$\text{NaCl} - \text{Na}_2\text{SO}_4^{52}$	-38	-318	-845

In the  $\text{NaCl-Na}_2\text{CO}_3$  system, it is evident from the negative  $\Delta G_{\text{MIX}}^E$  that there is an overall stabilizing effect upon mixing. The sign and magnitude of  $b_{01}$  indicate a net attractive energy gained in new interactions between  $\text{Cl}^-$  and  $\text{CO}_3^{-2}$ . The sign of  $b_{02}$  and  $b_{12}$  indicate unfavorable ternary interactions.

### Pitzer Treatment

In the lower half of Tables 11 and 14 are the results of the Pitzer treatment on the two systems studied. One recalls, from equation 4.12, that  $\Theta$  is an interaction parameter representing additional interactions between ions of like charge,  $\Theta'$  is its possible dependence on ionic strength, and  $\psi$  corresponds to new ternary interactions between two ions of like charge and one of opposite charge. It can be seen from the results of the  $\text{NaCl-SrCl}_2$  system that the Pitzer treatment fits the data quite well using only information derived from the single electrolytes. The addition of the  $\Theta_{\text{mixing}}$  parameter offers some improvement, and its sign is positive, analogous to the Scatchard  $b_{01}$  parameter. The results from the inclusion of additional mixing parameters are ambiguous, particularly since the  $\Theta$  parameter changes sign and magnitude drastically with only slight improvement in the standard deviation of fit. Without the need for parameters other than  $\Theta$ , the significance of the numbers below line 2 (lower half, Table 11), beyond being purely data-fitting coefficients, is questionable.



The results of the  $\text{NaCl-Na}_2\text{CO}_3$  system indicate that mixing parameters are necessary to fit the data reasonably, although the single electrolyte data alone produce a better fit than the Scatchard Treatment. Inclusion of  $\Theta$  improves the fit substantially; however, it is necessary to include  $\psi$  to attain the fit given by the Scatchard equation using  $b_{01}$ ,  $b_{02}$ , and  $b_{12}$ . It is obvious that there is no significant dependence of  $\Theta$  on ionic strength, hence no need for  $\Theta'$ . The signs of  $\Theta$  and  $\psi$  are consistent with Scatchard's  $b_{01}$  and  $b_{02}$  for the same system.

A computer program has been written for the calculation of the activity coefficients of the individual solutes from the appropriate form of the Pitzer equation,<sup>82</sup> (Appendix) utilizing the parameters from both the single electrolytes and the mixtures. For the  $\text{NaCl-SrCl}_2$  system, only the  $\Theta$  mixing term was used, and the results are given in Figure 8. The values for  $\gamma_{\text{NaCl}}^\circ$  were taken from Robinson and Stokes<sup>4</sup> while values for  $\gamma_{\text{SrCl}_2}^\circ$  were calculated from osmotic coefficient data on the single electrolytes. The positive change in excess free energy upon mixing is easily seen as an increase in the mean activity coefficient of  $\text{SrCl}_2$  which far outweighs the decrease in  $\gamma_{\text{NaCl}}$  exhibited at high ionic strength. The positive sign of the  $\Theta$  term in the Pitzer equation and of the  $b_{01}$  term in the Scatchard equation lead one to suspect that it is the strontium ion which is so highly affected upon mixing. This is reasonable, since no

new interactions arise between anions and cations. It is interesting that the sodium ion is barely affected, and only at high ionic strengths. Harned-type plots are given in Figure 9 for this system, and  $\log \gamma_{\pm}$  is seen to be a linear function of  $y$  for both electrolytes at all ionic strengths. This is to be expected, since the data were fitted adequately without any higher order terms in  $y$ , and  $\theta$  alone was used to generate the activity coefficients.

Figure 10 shows the activity coefficients in the mixture  $\text{NaCl}-\text{Na}_2\text{CO}_3$ . The negative excess free energy of mixing is evident here from a large decrease in  $\gamma_{\text{NaCl}}$  only slightly compensated for by the increase in  $\gamma_{\text{Na}_2\text{CO}_3}$ . The sign and magnitude of the mixing parameters point to the  $\text{Cl}^- - \text{CO}_3^{-2}$  interaction as the primary cause of the observed behavior. It can readily be seen also that addition of a large amount of  $\text{Na}_2\text{CO}_3$  to a smaller amount of  $\text{NaCl}$  will have a greater effect on  $\Delta G_{\text{MIX}}^{\text{E}}$  than the reverse operation. For example, in a situation where  $y_{\text{A}} = 0.15$  and  $y_{\text{B}} = 0.85$  at  $I = 3.0\text{m}$ , the calculated value of  $\Delta G_{\text{MIX}}^{\text{E}}$  is  $-439 \text{ J kg}^{-1}$ , whereas if  $y_{\text{A}} = 0.15$  and  $y_{\text{B}} = 0.85$ ,  $\Delta G_{\text{MIX}}^{\text{E}} = -332 \text{ J kg}^{-1}$ . The Harned plots (Figure 11) for this system introduce two important points. First, all the plots are linear except for  $\log \gamma_{\text{NaCl}}$  at high ionic strength. This gives evidence that it is to account for the behavior of  $\gamma_{\text{NaCl}}$  that we must introduce the higher order  $\psi$  term. Secondly, it appears that at lower ionic strengths, those which apply to seawater, the

data might adequately be fitted with the  $\Theta$  term alone. In this respect, they obey Harned's Rule. The intercept of  $\log \gamma_B$  at  $y_B = 0$  ( $y_A = 1$ ) at an ionic strength of 0.6m gives for the trace activity coefficient of  $\text{Na}_2\text{CO}_3$ ,  $\gamma_B^{\text{tr}} = 0.417$ . Using the estimate of 0.709 for  $\gamma_{\text{Na}^+}$  at  $I = 0.6\text{m}$  made by Robinson and Bates<sup>67</sup> one obtains 0.144 for  $\gamma_{\text{CO}_3^{2-}}$  which agrees closely with that estimated by Robinson.<sup>75</sup>

Figure 8. Mean activity coefficients of NaCl and  $\text{SrCl}_2$  as a function of ionic strength in the system  $\text{NaCl(A)} - \text{SrCl}_2(\text{B}) - \text{H}_2\text{O}$  for various ionic strength fractions,  $y_A$  and  $y_B$

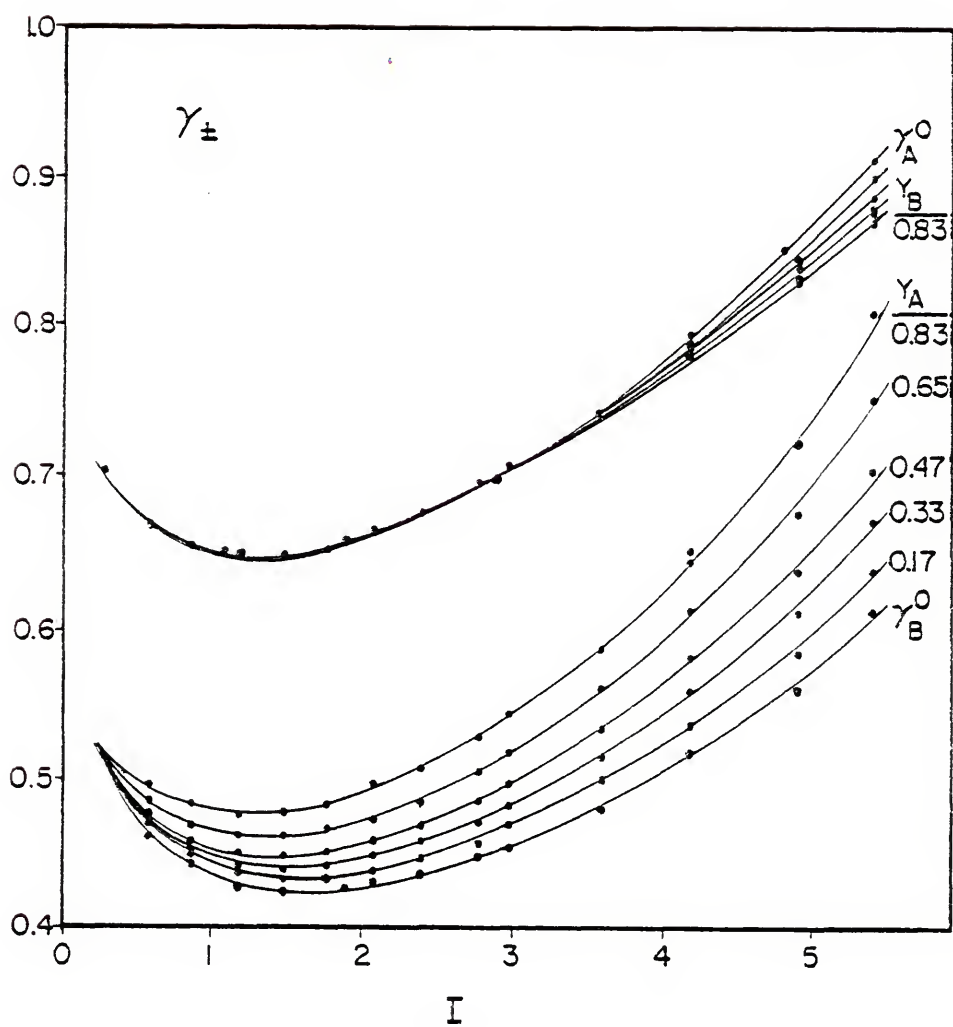


Figure 9. Harned plots for NaCl and  $\text{SrCl}_2$ ,  $-\log \gamma_{\pm}$  vs.  $y_B$ , in the system  $\text{NaCl(A)} - \text{SrCl}_2(\text{B}) - \text{H}_2\text{O}$

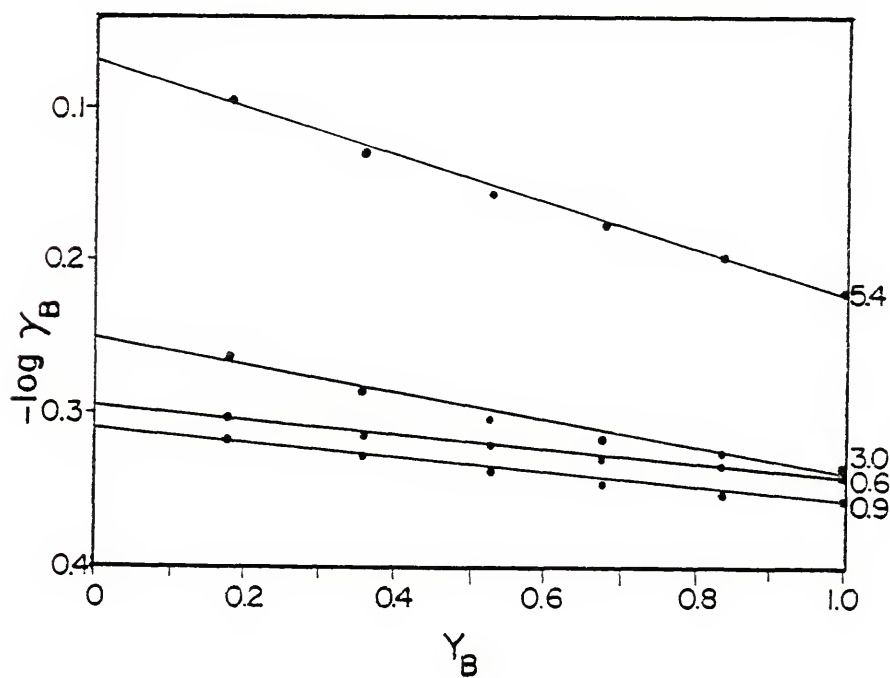
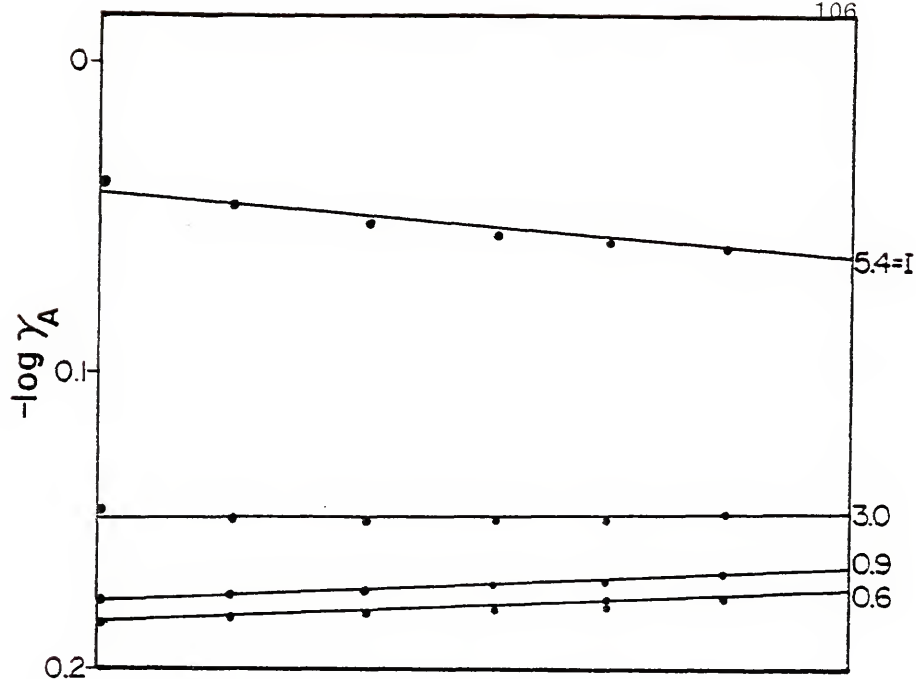


Figure 10. Mean activity coefficients of NaCl and Na<sub>2</sub>CO<sub>3</sub> as a function of ionic strength in the system NaCl(A) - Na<sub>2</sub>CO<sub>3</sub>(B) - H<sub>2</sub>O for various ionic strength fractions,  $y_A$  and  $y_B$



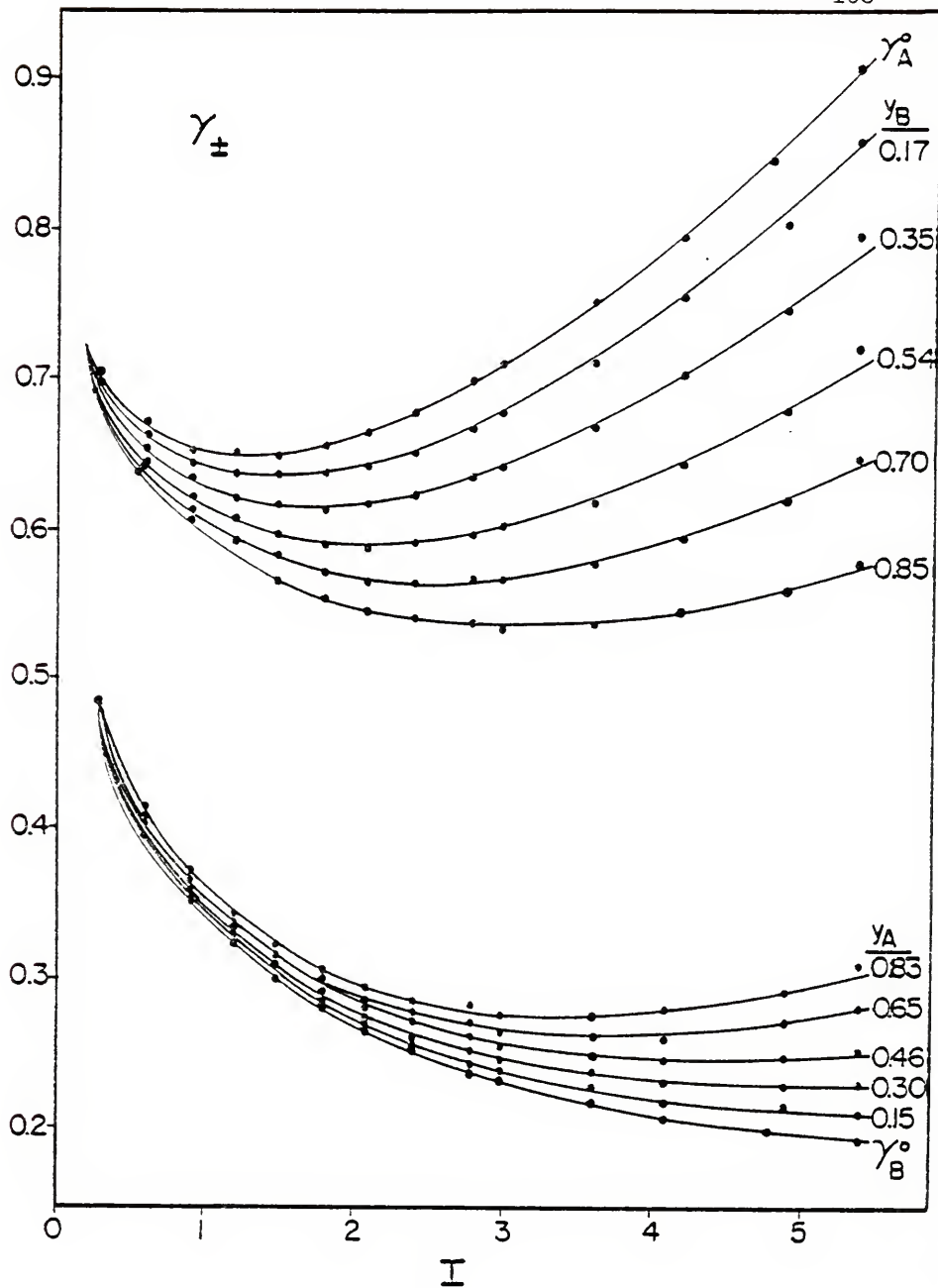
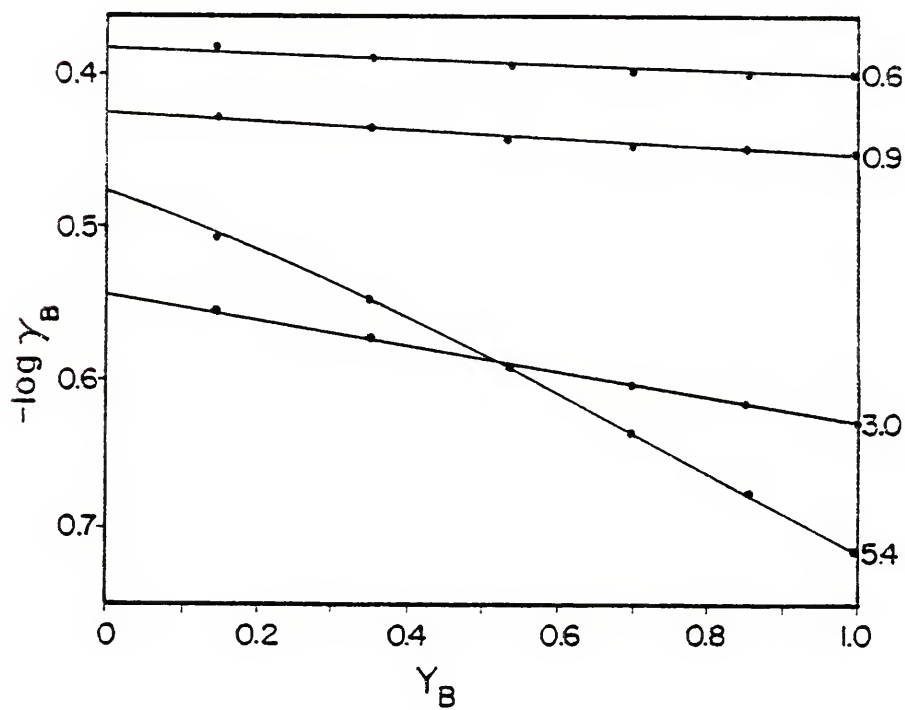
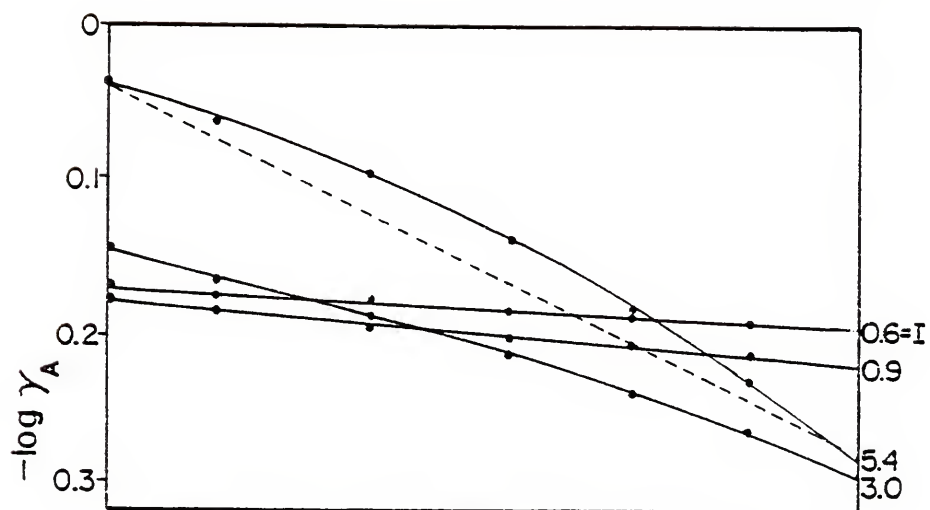


Figure 11. Harned plots for NaCl and Na<sub>2</sub>CO<sub>3</sub>,  $-\log \gamma_{\pm}$  vs.  $y_B$ , in the system NaCl(A) - Na<sub>2</sub>CO<sub>3</sub>(B) - H<sub>2</sub>O



## CHAPTER 8 CONCLUSIONS

The primary purpose of this research was to investigate the factors which affect the thermodynamic activity of individual species in complex saline mixtures. By utilizing a variety of experimental techniques on relatively simple systems of which complex mixtures (e.g., seawater) are composed, information can be obtained as to the specific influences on electrolyte behavior.

When the logarithm of the mean activity coefficient of HCl is plotted as a function of  $\gamma_{\text{MgCl}_2}$ , at ionic strengths corresponding to seawater, a straight line is obtained. When the slope of this line ("Harned Slope") is combined with the Harned Slope from a similar plot vs.  $\gamma_{\text{NaCl}}$ , weighting the two as to their molal ratio in natural seawater,  $\log \gamma_{\text{HCl}}$  behaves just as it has been found to do in total seawater excluding sulfate. In light of recent theoretical predictions concerning electrolyte mixtures, the linear decrease in  $\log \gamma_{\text{HCl}}$  appears to be due to interactions among the cations,  $\text{H}^+ - \text{Na}^+ - \text{Mg}^{+2}$ .

An adequate knowledge of the behavior of  $\text{H}^+$  in media of this sort allows the formulation of a pH scale for the standardization of pH measurements in seawater. With a

value for  $\gamma_{\text{HCl}}^{\text{tr}}$  and a reliable estimate of  $\gamma_{\text{HCl}}$  in seawater, a scale of  $\text{pm}_{\text{H}}$  in addition to  $\text{pa}_{\text{H}}$  is feasible. Further, examination of the residual liquid-junction effects which occur when a comparison is made of measurements in cells with liquid junction allows the estimation of the error which would result from pH measurement in seawater of a particular salinity when the glass electrode is standardized with a more dilute NBS phosphate buffer. This residual liquid-junction potential has been estimated to be about 4.3mV between the NBS 1:3.5 phosphate buffer ( $I = 0.1\text{m}$ ) and seawater of 35<sup>0</sup>/00 salinity ( $I = 0.67$ ) at 25°C. This amounts to about 0.07 pH unit.

It has been shown that residual liquid-junction potentials, which can cause errors of up to 0.05 pH unit in pH measurements in clinical media, can be eliminated by choice of a reference buffer where phosphate and NaCl contribute 0.06 and 0.10m, respectively, to the total ionic strength ( $I = 0.16\text{m}$ ,  $\text{pH}(\text{S}) = 7.297$  at 37°C). This  $\text{pH}(\text{S})$  value lies close to the NBS primary standard scale, and thus its adoption as a primary standard is practical. Secondary buffers of TES and HEPES with pH values above and below that of blood plasma have been proposed.

Finally, isopiestic studies have been made on two systems involving components present in seawater, in an attempt to shed light on the activity effects brought about by

mixing. Although current mixed electrolyte theories allow one to pinpoint the ions which have a primary effect on the free energy of the system, much work remains to be done to elucidate the nature of these interactions. Speaking only in terms of attractions and repulsions is an oversimplification at best. Trends exhibited in electrolyte behavior among elements in a periodic family, for example, lead one to suspect that ionic charge is only one factor and that ionic size and/or hydration capabilities are responsible for more specific phenomena. Debye and Hückel first noticed the need for an ion-size parameter, and this provided the foundation for all current treatments. The success of current theory in describing electrolyte behavior is formidable, and continued work can only lead to more useful descriptions of activity effects and, ideally, a unified theory which will provide a greater understanding of the nature of aqueous electrolyte behavior as a whole.

## APPENDIX

```

$JOB
C$PRINTON
C
C      JUNE 20, 1979  D. RICHARD WHITE, JR.
C
C      A PROGRAM FOR CALCULATING ACTIVITY COEFFICIENTS OF INDIVIDUAL
C      SOLUTES IN A MIXTURE OF A 1-1(A) AND A 1-2(B) ELECTROLYTE
C      BASED ON THE PITZER EQUATION, AND USING MIXING PARAMETERS
C      OBTAINED FROM OSMOTIC COEFFICIENT DATA.
C
1      REAL*8 SI(14),GZERO(14),GZEROB(14),ABO(14),ABI(14),BBO(14),BBI(14)
2      REAL*8 GAMA,GAMB,ABETA0,ABETA1,BBETA0,BBETA1,ACPHIA,BCPHIB
3      REAL*8 THETA, THETA1, PSI, YB(5), YA(5),DSORT,DLOG
4      100 FORMAT (3F9.6)
5      105 FORMAT (6F9.6)
6      110 FORMAT (5F9.6)
7      115 FORMAT ('1',20X,'ABO',20X,'BBO',10X,'ABI',10X,'BBI',)
8      120 FORMAT (20X,'LOG GAMMA A',10X,'LOG GAMMA B',10X,'YB',10X,'IS',)
9      125 FORMAT (20X,1F9.6,10X,1F9.6,10X,1F9.6,10X,1F9.6)
10     130 FORMAT (11)
11     C      GIVE THE COMPUTER I, GAMMA ZERO OF A, AND GAMMA ZERO OF B.
12     DO 1 J=1,14
13     READ (5,100) SI(J),GZERO(J),GZEROB(J)
14     C      GIVE THE COMPUTER SINGLE ELECTROLYTE DATA
15     READ (5,105) ABETA0,ABETA1,BBETA0,BBETA1,ACPHIA,BCPHIB
16     C      GIVE THE COMPUTER THE MIXING PARAMETERS
17     READ (5,105) THETA,THETA1,PSI
18     C      GIVE THE COMPUTER THE IONIC STRENGTH FRACTIONS OF B
19     READ (5,110) (YB(J),J=1,5)
20     DO 2 J=1,5
21     YA(J)=1-YB(J)
22     C      CONTINUE
23     WRITE (6,115)
24     C      COMPUTE B,S AND BI,S AT EACH IONIC STRENGTH BASED ON THE
25     C      RESPECTIVE BETA,S AND THEN PRINT
26     DO 3 J=1,14

```



```

22  ABO(J)=ABETA0+2*ABETA1*(1-(1+2*DSQRT(SI(J)))*(-2*DSQRT(SI(J))))
23  */(4*SI(J))
24  BBO(J)=BBETA0+2*BBETA1*(1-(1+2*DSQRT(SI(J)))*(-2*DSQRT(SI(J))))
25  */(4*SI(J))
26  ABI(J)=2*ABETA1*(-1+(1+2*DSQRT(SI(J))+2*SI(J))*(-2*DSQRT(SI(J))))
27  */(4*(SI(J)**2))
28  BBI(J)=2*BBETA1*(-1+(1+2*DSQRT(SI(J))+2*SI(J))*(-2*DSQRT(SI(J))))
29  */(4*(SI(J)**2))
30  WRITE (6,125) ABO(J),BBO(J),ABI(J),BBI(J)
31  CONTINUE
32  WRITE (6,120)
33
34  C      COMPUTE THE LOG GAMMA,S FOR A AND B AT EACH IONIC STRENGTH AND
35  C      THEN PRINT
36  C      DO 4 J=1,5
37  C      DO 5 K=1,14
38  C      GAMMA=DLOG10(GZERO(K))-1.4476D0*YB(J)*SI(K)*(4*ABO(K)-BBO(K)-THETA+
39  C      *SI(K)*(4*ABI(K)-BBI(K)-THETA1+5*ACPHIA-.707107D0*BCPHIB-PSI))
40  C      *-0.04825D0*(YB(J)**2)*(SI(K)**2)*(BBI(K)-3*ABI(K)+3*THETA1
41  C      *-3.5*ACPHIA-.707107D0*BCPHIB+2*PSI)
42  C      GAMB=DLOG10(GZEROB(K))+1.4476D0*YAC(J)*SI(K)*(4*ABO(K)-.66667D0*BBO
43  C      *(K)+2*THETA+SI(K)*(4*ABI(K)-.65667D0*BBI(K)+2*THETA1+1.3333D0*PSI
44  C      **2+.6667D0*ACPHIA))+1.4476D0*(YAC(J)**2)*(SI(K)**2)*(2*ABI(K)-.6666
45  C      *7D0*BBI(K)-PSI+.3333D0+1.3333D0*ACPHIA-BCPHIB*.2357D0-2*THETA1)
46  C      WRITE (6,125) GAMMA,GAMB,YB(J),SI(K)
47  C      CONTINUE
48  C      CONTINUE
49
50  C      REPEAT FOR NEXT PAIR OF ELECTROLYTES IF NECESSARY
51  C      READ (5,130) I
52  C      IF(I.EQ.1) GO TO 6
53  C      RETURN
54  C      END

```

\$ENTRY

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## BIOGRAPHICAL SKETCH

Donald Richard White, Jr., was born on September 5, 1953, in Washington, D. C. He attended the Montgomery County Public School System in Silver Spring, Maryland, through high school and was graduated in 1971.

In the fall of 1971, he entered Stetson University in DeLand, Florida, where he pursued a major in chemistry and a minor in secondary school education. During the summer of 1974, he was a participant in the National Science Foundation Undergraduate Research Program at the University of Florida. Awards received include the American Chemical Society Undergraduate Award in Analytical Chemistry, and the John F. Conn Award for outstanding undergraduate research. In 1975, he received the Bachelor of Science degree in chemistry and Florida Public School Certification to teach secondary level chemistry. He was employed as a research chemist at the Food and Drug Administration, Division of Drug Chemistry, in Washington, D. C., during the summer of 1975.

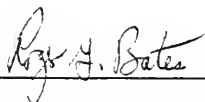
In the fall of 1975, he entered graduate school at the University of Florida with a teaching assistantship. He has since been doing research in solution chemistry, supported by the Oceanography Division of the National Science

Foundation, and under the supervision of Dr. Roger G. Bates. As part of his research activities, he spent 22 days aboard the research vessel, RV Gyre, investigating the utility of a fluoride ion selective electrode for the determination of interstitial fluoride in the Caribbean Sea.

White is a member of the American Chemical Society, Analytical Division, the Gamma Sigma Epsilon Chemical Fraternity, and the Sigma Xi Scientific Research Society, and is co-author of three publications.

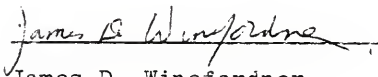


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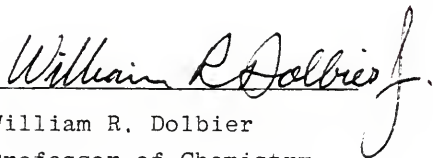
Roger G. Bates, Chairman  
Professor of Chemistry

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James D. Winefordner  
Professor of Chemistry

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William R. Dolbier  
Professor of Chemistry

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Patrick L. Brezonik

Patrick L. Brezonik  
Professor of Environmental  
Engineering Sciences

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 1979

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Dean, Graduate School